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(54) **ADVANCED CATALYSTS FOR AUTOMOTIVE APPLICATIONS**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

2,021,936 A 11/1935 Johnstone  
2,284,554 A 5/1942 Beyerstedt

(Continued)

FOREIGN PATENT DOCUMENTS

CN 1647858 A 8/2005  
CN 101011664 A 8/2007

(Continued)

OTHER PUBLICATIONS

Ahmad, K. et al. (2008). "Hybrid Nanocomposites: A New Route Towards Tougher Alumina Ceramics," *Composites Science and Technology* 68: 1321-1327.

(Continued)

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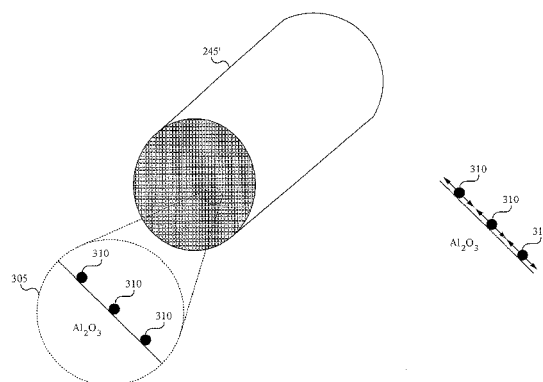
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(57) **ABSTRACT**

Embodiments of present inventions are directed to an advanced catalyst. The advanced catalyst includes a honeycomb structure with an at least one nano-particle on the honeycomb structure. The advanced catalyst used in diesel engines is a two-way catalyst. The advanced catalyst used in gas engines is a three-way catalyst. In both the two-way catalyst and the three-way catalyst, the at least one nano-particle includes nano-active material and nano-support. The nano-support is typically alumina. In the two-way catalyst, the nano-active material is platinum. In the three-way catalyst, the nano-active material is platinum, palladium, rhodium, or an alloy. The alloy is of platinum, palladium, and rhodium.

**34 Claims, 10 Drawing Sheets**



- (51) **Int. Cl.**
- |                   |           |             |         |                       |
|-------------------|-----------|-------------|---------|-----------------------|
| <b>B01J 23/08</b> | (2006.01) | 3,969,482 A | 7/1976  | Teller                |
| <b>B01J 23/40</b> | (2006.01) | 4,008,620 A | 2/1977  | Narato et al.         |
| <b>B01J 23/42</b> | (2006.01) | 4,018,388 A | 4/1977  | Andrews               |
| <b>B01J 23/44</b> | (2006.01) | 4,021,021 A | 5/1977  | Hall et al.           |
| <b>B01J 23/56</b> | (2006.01) | 4,127,760 A | 11/1978 | Meyer et al.          |
| <b>B01J 21/00</b> | (2006.01) | 4,139,497 A | 2/1979  | Castor et al.         |
| <b>B01J 21/04</b> | (2006.01) | 4,146,654 A | 3/1979  | Guyonnet              |
| <b>B01J 23/89</b> | (2006.01) | 4,157,316 A | 6/1979  | Thompson et al.       |
| <b>B01J 35/00</b> | (2006.01) | 4,171,288 A | 10/1979 | Keith et al.          |
| <b>B01J 37/00</b> | (2006.01) | 4,174,298 A | 11/1979 | Antos                 |
| <b>B01J 37/32</b> | (2006.01) | 4,189,925 A | 2/1980  | Long                  |
| <b>B01J 37/34</b> | (2006.01) | 4,227,928 A | 10/1980 | Wang                  |
| <b>B28B 23/00</b> | (2006.01) | 4,248,387 A | 2/1981  | Andrews               |
| <b>B32B 7/12</b>  | (2006.01) | 4,253,917 A | 3/1981  | Wang                  |
| <b>B32B 37/14</b> | (2006.01) | 4,260,649 A | 4/1981  | Dension et al.        |
| <b>B82Y 30/00</b> | (2011.01) | 4,284,609 A | 8/1981  | deVries               |
| <b>B82Y 40/00</b> | (2011.01) | 4,315,874 A | 2/1982  | Ushida et al.         |
| <b>C23C 4/12</b>  | (2006.01) | 4,326,492 A | 4/1982  | Leibbrand, Sr. et al. |
| <b>B01J 37/02</b> | (2006.01) | 4,344,779 A | 8/1982  | Isserlis              |
| <b>B01J 23/46</b> | (2006.01) | 4,369,167 A | 1/1983  | Weir                  |
|                   |           | 4,388,274 A | 6/1983  | Rourke et al.         |
|                   |           | 4,419,331 A | 12/1983 | Montalvo              |
|                   |           | 4,431,750 A | 2/1984  | McGinnis et al.       |
|                   |           | 4,436,075 A | 3/1984  | Campbell et al.       |
|                   |           | 4,440,733 A | 4/1984  | Lawson et al.         |
|                   |           | 4,458,138 A | 7/1984  | Adrian et al.         |
|                   |           | 4,459,327 A | 7/1984  | Wang                  |
|                   |           | 4,505,945 A | 3/1985  | Dubust et al.         |
|                   |           | 4,506,136 A | 3/1985  | Smyth et al.          |
|                   |           | 4,513,149 A | 4/1985  | Gray et al.           |
|                   |           | 4,523,981 A | 6/1985  | Ang et al.            |
|                   |           | 4,545,872 A | 10/1985 | Sammells et al.       |
|                   |           | RE32,244 E  | 9/1986  | Andersen              |
|                   |           | 4,609,441 A | 9/1986  | Frese, Jr. et al.     |
|                   |           | 4,610,857 A | 9/1986  | Ogawa et al.          |
|                   |           | 4,616,779 A | 10/1986 | Serrano et al.        |
|                   |           | 4,642,207 A | 2/1987  | Uda et al.            |
|                   |           | 4,723,589 A | 2/1988  | Iyer et al.           |
|                   |           | 4,731,517 A | 3/1988  | Cheney                |
|                   |           | 4,751,021 A | 6/1988  | Mollon et al.         |
|                   |           | 4,764,283 A | 8/1988  | Ashbrook et al.       |
|                   |           | 4,765,805 A | 8/1988  | Wahl et al.           |
|                   |           | 4,780,591 A | 10/1988 | Bernecki et al.       |
|                   |           | 4,824,624 A | 4/1989  | Palicka et al.        |
|                   |           | 4,836,084 A | 6/1989  | Vogelesang et al.     |
|                   |           | 4,855,505 A | 8/1989  | Koll                  |
|                   |           | 4,866,240 A | 9/1989  | Webber                |
|                   |           | 4,877,937 A | 10/1989 | Müller                |
|                   |           | 4,885,038 A | 12/1989 | Anderson et al.       |
|                   |           | 4,921,586 A | 5/1990  | Molter                |
|                   |           | 4,970,364 A | 11/1990 | Müller                |
|                   |           | 4,982,050 A | 1/1991  | Gammie et al.         |
|                   |           | 4,983,555 A | 1/1991  | Roy et al.            |
|                   |           | 4,987,033 A | 1/1991  | Abkowitz et al.       |
|                   |           | 5,006,163 A | 4/1991  | Benn et al.           |
|                   |           | 5,015,863 A | 5/1991  | Takeshima et al.      |
|                   |           | 5,041,713 A | 8/1991  | Weidman               |
|                   |           | 5,043,548 A | 8/1991  | Whitney et al.        |
|                   |           | 5,070,064 A | 12/1991 | Hsu et al.            |
|                   |           | 5,073,193 A | 12/1991 | Chaklader et al.      |
|                   |           | 5,133,190 A | 7/1992  | Abdelmalek            |
|                   |           | 5,151,296 A | 9/1992  | Tokunaga              |
|                   |           | 5,157,007 A | 10/1992 | Domesle et al.        |
|                   |           | 5,187,140 A | 2/1993  | Thorsteinson et al.   |
|                   |           | 5,192,130 A | 3/1993  | Endo et al.           |
|                   |           | 5,217,746 A | 6/1993  | Lenling et al.        |
|                   |           | 5,225,656 A | 7/1993  | Frind                 |
|                   |           | 5,230,844 A | 7/1993  | Macaire et al.        |
|                   |           | 5,233,153 A | 8/1993  | Coats                 |
|                   |           | 5,269,848 A | 12/1993 | Nakagawa              |
|                   |           | 5,294,242 A | 3/1994  | Zurecki et al.        |
|                   |           | 5,330,945 A | 7/1994  | Beckmeyer et al.      |
|                   |           | 5,338,716 A | 8/1994  | Triplett et al.       |
|                   |           | 5,357,075 A | 10/1994 | Muehlberger           |
|                   |           | 5,369,241 A | 11/1994 | Taylor et al.         |
|                   |           | 5,371,049 A | 12/1994 | Moffett et al.        |
|                   |           | 5,372,629 A | 12/1994 | Anderson et al.       |
|                   |           | 5,392,797 A | 2/1995  | Welch                 |
|                   |           | 5,436,080 A | 7/1995  | Inoue et al.          |
- (52) **U.S. Cl.**
- CPC ..... **B01J 35/0013** (2013.01); **B01J 37/00** (2013.01); **B01J 37/009** (2013.01); **B01J 37/0211** (2013.01); **B01J 37/32** (2013.01); **B01J 37/349** (2013.01); **B28B 23/0087** (2013.01); **B32B 7/12** (2013.01); **B32B 37/14** (2013.01); **B82Y 30/00** (2013.01); **B82Y 40/00** (2013.01); **C23C 4/127** (2013.01); **Y02T 10/22** (2013.01)
- (56) **References Cited**
- U.S. PATENT DOCUMENTS
- |               |         |   |
|---------------|---------|---|
| 2,419,042 A   | 4/1947  | Todd                                    |
| 2,519,531 A   | 8/1950  | Worn                                    |
| 2,562,753 A   | 7/1951  | Trost                                   |
| 2,689,780 A   | 9/1954  | Rice                                    |
| 3,001,402 A   | 9/1961  | Koblin                                  |
| 3,042,511 A   | 7/1962  | Reding, Jr.                             |
| 3,067,025 A   | 12/1962 | Chisholm                                |
| 3,145,287 A   | 8/1964  | Siebein et al.                          |
| 3,178,121 A   | 4/1965  | Wallace, Jr.                            |
| 3,179,782 A   | 4/1965  | Matvay                                  |
| 3,181,947 A   | 5/1965  | Vordahl                                 |
| 3,235,700 A   | 2/1966  | Mondain-Monval et al.                   |
| 3,313,908 A   | 4/1967  | Unger et al.                            |
| 3,387,110 A   | 6/1968  | Wendler et al.                          |
| 3,401,465 A   | 9/1968  | Larwill                                 |
| 3,450,926 A   | 6/1969  | Kiernan                                 |
| 3,457,788 A   | 7/1969  | Nobuo Miyajima                          |
| 3,520,656 A   | 7/1970  | Yates et al.                            |
| 3,537,513 A   | 11/1970 | Austin                                  |
| 3,552,653 A   | 1/1971  | Inoue                                   |
| 3,617,358 A   | 11/1971 | Dittrich                                |
| 3,667,111 A   | 6/1972  | Chartet                                 |
| 3,730,827 A   | 5/1973  | Matchen et al.                          |
| 3,741,001 A   | 6/1973  | Fletcher et al.                         |
| 3,743,708 A * | 7/1973  | Chase et al. .... B82Y 30/00<br>423/617 |
| 3,752,172 A   | 8/1973  | Cohen et al.                            |
| 3,761,360 A   | 9/1973  | Auvil et al.                            |
| 3,774,442 A   | 11/1973 | Gustaysson                              |
| 3,804,034 A   | 4/1974  | Stiglich, Jr.                           |
| 3,830,756 A   | 8/1974  | Sanchez et al.                          |
| 3,857,744 A   | 12/1974 | Moss                                    |
| 3,871,448 A   | 3/1975  | Vann et al.                             |
| 3,892,882 A   | 7/1975  | Guest et al.                            |
| 3,914,573 A   | 10/1975 | Muehlberger                             |
| 3,959,094 A   | 5/1976  | Steinberg                               |
| 3,959,420 A   | 5/1976  | Geddes et al.                           |

(56)

## References Cited

## U.S. PATENT DOCUMENTS

5,439,865 A	8/1995	Abe et al.	6,413,898 B1	7/2002	Faber et al.
5,442,153 A	8/1995	Marantz et al.	6,416,818 B1	7/2002	Aikens et al.
5,452,854 A	9/1995	Keller	RE37,853 E	9/2002	Detering et al.
5,460,701 A	10/1995	Parker et al.	6,444,009 B1	9/2002	Liu et al.
5,464,458 A	11/1995	Yamamoto	6,475,951 B1	11/2002	Domesle et al.
5,485,941 A	1/1996	Guyomard et al.	6,488,904 B1	12/2002	Cox et al.
5,486,675 A	1/1996	Taylor et al.	6,491,423 B1	12/2002	Skibo et al.
5,489,449 A	2/1996	Umeya et al.	6,506,995 B1	1/2003	Fusaro, Jr. et al.
5,510,086 A	4/1996	Hemingway et al.	6,517,800 B1	2/2003	Cheng et al.
5,534,149 A	7/1996	Birkenbeil et al.	6,524,662 B2	2/2003	Jang et al.
5,534,270 A	7/1996	De Castro	6,531,704 B2	3/2003	Yadav et al.
5,543,173 A	8/1996	Horn, Jr. et al.	6,548,445 B1	4/2003	Buysch et al.
5,553,507 A	9/1996	Basch et al.	6,554,609 B2	4/2003	Yadav et al.
5,558,771 A	9/1996	Hagen et al.	6,562,304 B1	5/2003	Mizrahi
5,562,966 A	10/1996	Clarke et al.	6,562,495 B2	5/2003	Yadav et al.
5,582,807 A	12/1996	Liao et al.	6,569,393 B1	5/2003	Hoke et al.
5,596,973 A	1/1997	Grice	6,569,397 B1	5/2003	Yadav et al.
5,611,896 A	3/1997	Swanepoel et al.	6,569,518 B2	5/2003	Yadav et al.
5,630,322 A	5/1997	Heilmann et al.	6,572,672 B2	6/2003	Yadav et al.
5,652,304 A	7/1997	Calderon et al.	6,579,446 B1	6/2003	Teran et al.
5,714,644 A	2/1998	Irgang et al.	6,596,187 B2	7/2003	Coll et al.
5,723,027 A	3/1998	Serole	6,603,038 B1	8/2003	Hagemeyer et al.
5,723,187 A	3/1998	Popoola et al.	6,607,821 B2	8/2003	Yadav et al.
5,726,414 A	3/1998	Kitahashi et al.	6,610,355 B2	8/2003	Yadav et al.
5,733,662 A	3/1998	Bogachek	6,623,559 B2	9/2003	Huang
5,749,938 A	5/1998	Coombs	6,635,357 B2	10/2003	Moxson et al.
5,776,359 A	7/1998	Schultz et al.	6,641,775 B2	11/2003	Vigliotti et al.
5,788,738 A	8/1998	Pirzada et al.	6,652,822 B2	11/2003	Phillips et al.
5,804,155 A	9/1998	Farrauto et al.	6,652,967 B2	11/2003	Yadav et al.
5,811,187 A	9/1998	Anderson et al.	6,669,823 B1	12/2003	Sarkas et al.
5,837,959 A	11/1998	Muehlberger et al.	6,682,002 B2	1/2004	Kyotani
5,851,507 A	12/1998	Pirzada et al.	6,689,192 B1	2/2004	Phillips et al.
5,853,815 A	12/1998	Muehlberger	6,699,398 B1	3/2004	Kim
5,858,470 A	1/1999	Bernecki et al.	6,706,097 B2	3/2004	Zomes
5,884,473 A	3/1999	Noda et al.	6,706,660 B2	3/2004	Park
5,905,000 A	5/1999	Yadav et al.	6,710,207 B2	3/2004	Bogan, Jr. et al.
5,928,806 A	7/1999	Olah et al.	6,713,176 B2	3/2004	Yadav et al.
5,935,293 A	8/1999	Detering et al.	6,716,525 B1	4/2004	Yadav et al.
5,973,289 A	10/1999	Read et al.	6,744,006 B2	6/2004	Johnson et al.
5,989,648 A	11/1999	Phillips	6,746,791 B2	6/2004	Yadav et al.
5,993,967 A	11/1999	Brotzman, Jr. et al.	6,772,584 B2	8/2004	Chun et al.
5,993,988 A	11/1999	Ohara et al.	6,780,350 B1 *	8/2004	Kodas ..... B01J 2/02 257/E21.304
6,004,620 A	12/1999	Camm	6,786,950 B2	9/2004	Yadav et al.
6,012,647 A	1/2000	Ruta et al.	6,813,931 B2	11/2004	Yadav et al.
6,033,781 A	3/2000	Brotzman, Jr. et al.	6,817,388 B2	11/2004	Tsangaris et al.
6,045,765 A	4/2000	Nakatsuji et al.	6,832,735 B2	12/2004	Yadav et al.
6,059,853 A	5/2000	Coombs	6,838,072 B1	1/2005	Kong et al.
6,066,587 A	5/2000	Kurokawa et al.	6,841,509 B1	1/2005	Hwang et al.
6,084,197 A	7/2000	Fusaro, Jr.	6,855,410 B2	2/2005	Buckley
6,093,306 A	7/2000	Hanrahan et al.	6,855,426 B2	2/2005	Yadav
6,093,378 A	7/2000	Deeba et al.	6,855,749 B1	2/2005	Yadav et al.
6,102,106 A	8/2000	Manning et al.	6,858,170 B2	2/2005	Van Thillo et al.
6,117,376 A	9/2000	Merkel	6,886,545 B1	5/2005	Holm
6,139,813 A	10/2000	Narula et al.	6,891,319 B2	5/2005	Dean et al.
6,140,539 A	10/2000	Sander et al.	6,896,958 B1	5/2005	Cayton et al.
6,168,694 B1	1/2001	Huang et al.	6,902,699 B2	6/2005	Fritzemeier et al.
6,190,627 B1	2/2001	Hoke et al.	6,916,872 B2	7/2005	Yadav et al.
6,213,049 B1	4/2001	Yang	6,919,065 B2	7/2005	Zhou et al.
6,214,195 B1	4/2001	Yadav et al.	6,919,527 B2	7/2005	Boulos et al.
6,228,904 B1	5/2001	Yadav et al.	6,933,331 B2	8/2005	Yadav et al.
6,231,792 B1	5/2001	Overbeek et al.	6,972,115 B1	12/2005	Ballard
6,254,940 B1	7/2001	Pratsinis et al.	6,986,877 B2	1/2006	Takikawa et al.
6,261,484 B1	7/2001	Phillips et al.	6,994,837 B2	2/2006	Boulos et al.
6,267,864 B1	7/2001	Yadav et al.	7,007,872 B2	3/2006	Yadav et al.
6,322,756 B1	11/2001	Arno et al.	7,022,305 B2	4/2006	Drumm et al.
6,342,465 B1	1/2002	Klein et al.	7,052,777 B2	5/2006	Brotzman, Jr. et al.
6,344,271 B1	2/2002	Yadav et al.	7,066,976 B2 *	6/2006	Hampden-Smith ..... B01J 2/02 257/E23.075
6,362,449 B1	3/2002	Hadidi et al.	7,073,559 B2	7/2006	O'Larey et al.
6,379,419 B1	4/2002	Celik et al.	7,074,364 B2	7/2006	Jahn et al.
6,387,560 B1	5/2002	Yadav et al.	7,081,267 B2	7/2006	Yadav
6,395,214 B1	5/2002	Kear et al.	7,094,370 B2 *	8/2006	Kodas ..... B01J 2/02 257/E23.075
6,398,843 B1	6/2002	Tarrant	7,101,819 B2	9/2006	Rosenflanz et al.
6,399,030 B1	6/2002	Nolan	7,147,544 B2	12/2006	Rosenflanz
6,409,851 B1	6/2002	Sethuram et al.	7,147,894 B2	12/2006	Zhou et al.
6,413,781 B1	7/2002	Geis et al.	7,166,198 B2	1/2007	Van Der Walt et al.
			7,166,663 B2	1/2007	Cayton et al.

(56)

**References Cited**

## U.S. PATENT DOCUMENTS

7,172,649 B2	2/2007	Conrad et al.	8,574,408 B2	11/2013	Layman
7,172,790 B2	2/2007	Koulik et al.	8,574,520 B2	11/2013	Koplin et al.
7,178,747 B2	2/2007	Yadav et al.	8,575,059 B1	11/2013	Biberger et al.
7,208,126 B2	4/2007	Musick et al.	8,604,398 B1	12/2013	Layman
7,211,236 B2	5/2007	Stark et al.	8,652,992 B2	2/2014	Yin et al.
7,217,407 B2	5/2007	Zhang	8,668,803 B1	3/2014	Biberger
7,220,398 B2	5/2007	Sutorik et al.	8,669,202 B2	3/2014	van den Hoek et al.
7,255,498 B2	8/2007	Bush et al.	8,679,433 B2	3/2014	Yin et al.
7,265,076 B2	9/2007	Taguchi et al.	8,821,786 B1	9/2014	Biberger
7,282,167 B2	10/2007	Carpenter	8,828,328 B1	9/2014	Leamon et al.
7,307,195 B2	12/2007	Polverejan et al.	8,859,035 B1	10/2014	Leamon
7,323,655 B2	1/2008	Kim	8,877,357 B1	11/2014	Biberger
7,384,447 B2	6/2008	Kodas et al.	8,893,651 B1	11/2014	Biberger et al.
7,402,899 B1	7/2008	Whiting et al.	8,906,498 B1	12/2014	Biberger
7,417,008 B2	8/2008	Richards et al.	8,927,403 B2 *	1/2015	Huotari ..... H01L 21/28079 438/584
7,494,527 B2	2/2009	Jurewicz et al.	8,932,514 B1	1/2015	Yin et al.
7,507,495 B2	3/2009	Wang et al.	8,992,820 B1	3/2015	Yin et al.
7,517,826 B2	4/2009	Fujdala et al.	9,023,754 B2	5/2015	Biberger
7,534,738 B2	5/2009	Fujdala et al.	9,039,916 B1	5/2015	Lehman, Jr.
7,541,012 B2	6/2009	Yeung et al.	9,089,840 B2	7/2015	Biberger et al.
7,541,310 B2	6/2009	Espinoza et al.	9,090,475 B1	7/2015	Lehman, Jr.
7,557,324 B2	7/2009	Nylen et al.	9,119,309 B1	8/2015	Lehman, Jr.
7,572,315 B2	8/2009	Boulos et al.	9,126,191 B2	9/2015	Yin et al.
7,576,029 B2	8/2009	Saito et al.	9,132,404 B2	9/2015	Layman
7,576,031 B2	8/2009	Beutel et al.	9,149,797 B2	10/2015	Leamon
7,601,294 B2	10/2009	Ripley et al.	9,156,025 B2	10/2015	Qi et al.
7,604,843 B1	10/2009	Robinson et al.	9,180,423 B2	11/2015	Biberger et al.
7,611,686 B2	11/2009	Alekseeva et al.	2001/0004009 A1	6/2001	MacKelvie
7,615,097 B2	11/2009	McKeclutie et al.	2001/0042802 A1	11/2001	Youds
7,618,919 B2	11/2009	Shimazu et al.	2001/0055554 A1	12/2001	Hoke et al.
7,622,693 B2	11/2009	Foret	2002/0018815 A1	2/2002	Sievers et al.
7,632,775 B2	12/2009	Zhou et al.	2002/0068026 A1	6/2002	Murrell et al.
7,635,218 B1	12/2009	Lott	2002/0071800 A1	6/2002	Hoke et al.
7,674,744 B2	3/2010	Shiratori et al.	2002/0079620 A1	6/2002	DuBuis et al.
7,678,419 B2	3/2010	Kevwitch et al.	2002/0100751 A1	8/2002	Carr
7,704,369 B2	4/2010	Olah et al.	2002/0102674 A1	8/2002	Anderson
7,709,411 B2	5/2010	Zhou et al.	2002/0131914 A1	9/2002	Sung
7,709,414 B2	5/2010	Fujdala et al.	2002/0143417 A1	10/2002	Ito et al.
7,745,367 B2	6/2010	Fujdala et al.	2002/0168466 A1	11/2002	Tapphorn et al.
7,750,265 B2	7/2010	Belashchenko et al.	2002/0182735 A1	12/2002	Kibby et al.
7,759,279 B2	7/2010	Shiratori et al.	2002/0183191 A1	12/2002	Faber et al.
7,759,281 B2	7/2010	Kezuka et al.	2002/0192129 A1	12/2002	Shamouilian et al.
7,803,210 B2	9/2010	Sekine et al.	2003/0036786 A1	2/2003	Duren et al.
7,842,515 B2	11/2010	Zou et al.	2003/0042232 A1	3/2003	Shimazu
7,851,405 B2	12/2010	Wakamatsu et al.	2003/0047617 A1	3/2003	Shanmugham et al.
7,874,239 B2	1/2011	Howland	2003/0066800 A1	4/2003	Saim et al.
7,875,573 B2	1/2011	Beutel et al.	2003/0085663 A1	5/2003	Horsky
7,897,127 B2	3/2011	Layman et al.	2003/0102099 A1	6/2003	Yadav et al.
7,902,104 B2	3/2011	Kalck	2003/0108459 A1	6/2003	Wu et al.
7,905,942 B1	3/2011	Layman	2003/0110931 A1	6/2003	Aghajanian et al.
7,935,655 B2	5/2011	Tolmachev	2003/0129098 A1	7/2003	Endo et al.
7,951,428 B2	5/2011	Hoerr et al.	2003/0139288 A1	7/2003	Cai et al.
8,003,020 B2	8/2011	Jankowiak et al.	2003/0143153 A1	7/2003	Boulos et al.
8,051,724 B1	11/2011	Layman et al.	2003/0172772 A1	9/2003	Sethuram et al.
8,076,258 B1	12/2011	Biberger	2003/0223546 A1	12/2003	McGregor et al.
8,080,494 B2	12/2011	Yasuda et al.	2004/0009118 A1	1/2004	Phillips et al.
8,089,495 B2	1/2012	Keller	2004/0023302 A1	2/2004	Archibald et al.
8,129,654 B2	3/2012	Lee et al.	2004/0023453 A1	2/2004	Xu et al.
8,142,619 B2	3/2012	Layman et al.	2004/0065170 A1	4/2004	Wu et al.
8,168,561 B2	5/2012	Virkar	2004/0077494 A1	4/2004	LaBarge et al.
8,173,572 B2	5/2012	Feaviour	2004/0103751 A1	6/2004	Joseph et al.
8,211,392 B2	7/2012	Grubert et al.	2004/0109523 A1	6/2004	Singh et al.
8,258,070 B2	9/2012	Fujdala et al.	2004/0119064 A1	6/2004	Narayan et al.
8,278,240 B2	10/2012	Tange et al.	2004/0127586 A1	7/2004	Jin et al.
8,294,060 B2	10/2012	Mohanty et al.	2004/0129222 A1	7/2004	Nylen et al.
8,309,489 B2	11/2012	Roldan Cuenya et al.	2004/0166036 A1	8/2004	Chen et al.
8,349,761 B2	1/2013	Xia et al.	2004/0167009 A1	8/2004	Kuntz et al.
8,404,611 B2	3/2013	Nakamura et al.	2004/0176246 A1	9/2004	Shirk et al.
8,470,112 B1	6/2013	Biberger	2004/0208805 A1	10/2004	Fincke et al.
8,481,449 B1	7/2013	Biberger et al.	2004/0213998 A1	10/2004	Hearley et al.
8,507,401 B1	8/2013	Biberger et al.	2004/0235657 A1	11/2004	Xiao et al.
8,507,402 B1	8/2013	Biberger et al.	2004/0238345 A1	12/2004	Koulik et al.
8,524,631 B2	9/2013	Biberger	2004/0251017 A1	12/2004	Pillion et al.
8,545,652 B1	10/2013	Biberger	2004/0251241 A1	12/2004	Blutke et al.
8,557,727 B2	10/2013	Yin et al.	2005/0000321 A1	1/2005	O'Larey et al.
			2005/0000950 A1	1/2005	Schroder et al.
			2005/0058797 A1	3/2005	Sen et al.
			2005/0066805 A1	3/2005	Park et al.

(56)

## References Cited

## U.S. PATENT DOCUMENTS

- |                  |         |   |                 |         |                      |
|------------------|---------|---|-----------------|---------|----------------------|
| 2005/0070431 A1  | 3/2005  | Alvin et al.                                | 2008/0207858 A1 | 8/2008  | Kowaleski et al.     |
| 2005/0077034 A1  | 4/2005  | King  | 2008/0248704 A1 | 10/2008 | Mathis et al.        |
| 2005/0097988 A1  | 5/2005  | Kodas et al.                                | 2008/0274344 A1 | 11/2008 | Vieth et al.         |
| 2005/0106865 A1  | 5/2005  | Chung et al.                                | 2008/0277092 A1 | 11/2008 | Layman et al.        |
| 2005/0133121 A1  | 6/2005  | Subramanian et al.                          | 2008/0277264 A1 | 11/2008 | Sprague              |
| 2005/0153069 A1  | 7/2005  | Tapphorn et al.                             | 2008/0277266 A1 | 11/2008 | Layman               |
| 2005/0163673 A1  | 7/2005  | Johnson et al.                              | 2008/0277267 A1 | 11/2008 | Biberger et al.      |
| 2005/0199739 A1  | 9/2005  | Kuroda et al.                               | 2008/0277268 A1 | 11/2008 | Layman               |
| 2005/0211018 A1  | 9/2005  | Jurewicz et al.                             | 2008/0277269 A1 | 11/2008 | Layman et al.        |
| 2005/0220695 A1  | 10/2005 | Abatzoglou et al.                           | 2008/0277270 A1 | 11/2008 | Biberger et al.      |
| 2005/0227864 A1  | 10/2005 | Sutorik et al.                              | 2008/0277271 A1 | 11/2008 | Layman               |
| 2005/0233380 A1  | 10/2005 | Pesiri et al.                               | 2008/0280049 A1 | 11/2008 | Kevwitch et al.      |
| 2005/0240069 A1  | 10/2005 | Polverejan et al.                           | 2008/0280751 A1 | 11/2008 | Harutyunyan et al.   |
| 2005/0258766 A1  | 11/2005 | Kim   | 2008/0280756 A1 | 11/2008 | Biberger et al.      |
| 2005/0274646 A1  | 12/2005 | Lawson et al.                               | 2008/0283411 A1 | 11/2008 | Eastman et al.       |
| 2005/0275143 A1  | 12/2005 | Toth  | 2008/0283498 A1 | 11/2008 | Yamazaki             |
| 2006/0043651 A1  | 3/2006  | Yamamoto et al.                             | 2008/0307960 A1 | 12/2008 | Hendrickson et al.   |
| 2006/0051505 A1  | 3/2006  | Kortshagen et al.                           | 2009/0010801 A1 | 1/2009  | Murphy et al.        |
| 2006/0068989 A1  | 3/2006  | Ninomiya et al.                             | 2009/0018008 A1 | 1/2009  | Jankowiak et al.     |
| 2006/0094595 A1  | 5/2006  | Labarge                                     | 2009/0054230 A1 | 2/2009  | Veeraraghavan et al. |
| 2006/0096393 A1  | 5/2006  | Pesiri                                      | 2009/0081092 A1 | 3/2009  | Yang et al.          |
| 2006/0105910 A1  | 5/2006  | Zhou et al.                                 | 2009/0088585 A1 | 4/2009  | Schammel et al.      |
| 2006/0108332 A1  | 5/2006  | Belashchenko                                | 2009/0092887 A1 | 4/2009  | McGrath et al.       |
| 2006/0153728 A1  | 7/2006  | Schoenung et al.                            | 2009/0098402 A1 | 4/2009  | Kang et al.          |
| 2006/0153765 A1  | 7/2006  | Pham-Huu et al.                             | 2009/0114568 A1 | 5/2009  | Trevino et al.       |
| 2006/0159596 A1  | 7/2006  | De La Veaux et al.                          | 2009/0162991 A1 | 6/2009  | Beneyton et al.      |
| 2006/0166809 A1  | 7/2006  | Malek et al.                                | 2009/0168506 A1 | 7/2009  | Han et al.           |
| 2006/0211569 A1  | 9/2006  | Dang et al.                                 | 2009/0170242 A1 | 7/2009  | Lin et al.           |
| 2006/0213326 A1  | 9/2006  | Gollob et al.                               | 2009/0181474 A1 | 7/2009  | Nagai                |
| 2006/0222780 A1  | 10/2006 | Gurevich et al.                             | 2009/0200180 A1 | 8/2009  | Capote et al.        |
| 2006/0231525 A1  | 10/2006 | Asakawa et al.                              | 2009/0208367 A1 | 8/2009  | Calio et al.         |
| 2007/0014919 A1* | 1/2007  | Hamalainen ..... C23C 16/45525<br>427/248.1 | 2009/0209408 A1 | 8/2009  | Kitamura et al.      |
| 2007/0020167 A1  | 1/2007  | Han et al.                                  | 2009/0223410 A1 | 9/2009  | Jun et al.           |
| 2007/0044513 A1  | 3/2007  | Kear et al.                                 | 2009/0238736 A1 | 9/2009  | Takahashi            |
| 2007/0048206 A1  | 3/2007  | Hung et al.                                 | 2009/0253037 A1 | 10/2009 | Park et al.          |
| 2007/0049484 A1  | 3/2007  | Kear et al.                                 | 2009/0274897 A1 | 11/2009 | Kaner et al.         |
| 2007/0063364 A1  | 3/2007  | Hsiao et al.                                | 2009/0274903 A1 | 11/2009 | Addiego              |
| 2007/0084308 A1  | 4/2007  | Nakamura et al.                             | 2009/0286899 A1 | 11/2009 | Hofmann et al.       |
| 2007/0084834 A1  | 4/2007  | Hanus et al.                                | 2009/0320449 A1 | 12/2009 | Beutel et al.        |
| 2007/0087934 A1  | 4/2007  | Martens et al.                              | 2009/0324468 A1 | 12/2009 | Golden et al.        |
| 2007/0092768 A1  | 4/2007  | Lee et al.                                  | 2010/0050868 A1 | 3/2010  | Kuznicki et al.      |
| 2007/0153390 A1  | 7/2007  | Nakamura et al.                             | 2010/0089002 A1 | 4/2010  | Merkel               |
| 2007/0161506 A1  | 7/2007  | Saito et al.                                | 2010/0092358 A1 | 4/2010  | Koegel et al.        |
| 2007/0163385 A1  | 7/2007  | Takahashi et al.                            | 2010/0124514 A1 | 5/2010  | Chelluri et al.      |
| 2007/0172721 A1  | 7/2007  | Pak et al.                                  | 2010/0166629 A1 | 7/2010  | Deeba                |
| 2007/0173403 A1  | 7/2007  | Koike et al.                                | 2010/0180581 A1 | 7/2010  | Grubert et al.       |
| 2007/0178673 A1  | 8/2007  | Gole et al.                                 | 2010/0180582 A1 | 7/2010  | Mueller-Stach et al. |
| 2007/0221404 A1  | 9/2007  | Das et al.                                  | 2010/0186375 A1 | 7/2010  | Kazi et al.          |
| 2007/0253874 A1  | 11/2007 | Foret                                       | 2010/0240525 A1 | 9/2010  | Golden et al.        |
| 2007/0259768 A1* | 11/2007 | Kear ..... C04B 35/117<br>501/120           | 2010/0260652 A1 | 10/2010 | Nakane et al.        |
| 2007/0266825 A1  | 11/2007 | Ripley et al.                               | 2010/0275781 A1 | 11/2010 | Tsangaris            |
| 2007/0292321 A1  | 12/2007 | Plischke et al.                             | 2010/0323118 A1 | 12/2010 | Mohanty et al.       |
| 2008/0006954 A1  | 1/2008  | Yubuta et al.                               | 2011/0006463 A1 | 1/2011  | Layman               |
| 2008/0026041 A1  | 1/2008  | Tepper et al.                               | 2011/0030346 A1 | 2/2011  | Neubauer et al.      |
| 2008/0026932 A1  | 1/2008  | Satoh et al.                                | 2011/0049045 A1 | 3/2011  | Hurt et al.          |
| 2008/0031806 A1  | 2/2008  | Gavenonis et al.                            | 2011/0052467 A1 | 3/2011  | Chase et al.         |
| 2008/0038578 A1  | 2/2008  | Li  | 2011/0143041 A1 | 6/2011  | Layman et al.        |
| 2008/0045405 A1  | 2/2008  | Beutel et al.                               | 2011/0143915 A1 | 6/2011  | Yin et al.           |
| 2008/0047261 A1  | 2/2008  | Han et al.                                  | 2011/0143916 A1 | 6/2011  | Leamon               |
| 2008/0056977 A1  | 3/2008  | Hung et al.                                 | 2011/0143926 A1 | 6/2011  | Yin et al.           |
| 2008/0057212 A1  | 3/2008  | Dorier et al.                               | 2011/0143930 A1 | 6/2011  | Yin et al.           |
| 2008/0064769 A1  | 3/2008  | Sato et al.                                 | 2011/0143933 A1 | 6/2011  | Yin et al.           |
| 2008/0104735 A1  | 5/2008  | Howland                                     | 2011/0144382 A1 | 6/2011  | Yin et al.           |
| 2008/0105083 A1  | 5/2008  | Nakamura et al.                             | 2011/0152550 A1 | 6/2011  | Grey et al.          |
| 2008/0108005 A1  | 5/2008  | Carpenter                                   | 2011/0154807 A1 | 6/2011  | Chandler et al.      |
| 2008/0116178 A1  | 5/2008  | Weidman                                     | 2011/0158871 A1 | 6/2011  | Arnold et al.        |
| 2008/0125308 A1  | 5/2008  | Fujdala et al.                              | 2011/0174604 A1 | 7/2011  | Diesel et al.        |
| 2008/0125313 A1  | 5/2008  | Fujdala et al.                              | 2011/0243808 A1 | 10/2011 | Fossey et al.        |
| 2008/0138651 A1  | 6/2008  | Doi et al.                                  | 2011/0245073 A1 | 10/2011 | Oljaca et al.        |
| 2008/0175936 A1  | 7/2008  | Tokita et al.                               | 2011/0247336 A9 | 10/2011 | Farsad et al.        |
| 2008/0187714 A1  | 8/2008  | Wakamatsu et al.                            | 2011/0271658 A1 | 11/2011 | Hoyer et al.         |
| 2008/0202288 A1  | 8/2008  | McKechnie et al.                            | 2011/0305612 A1 | 12/2011 | Müller-Stach et al.  |
| 2008/0206562 A1  | 8/2008  | Stucky et al.                               | 2012/0023909 A1 | 2/2012  | Lambert et al.       |
|                  |         |   | 2012/0045373 A1 | 2/2012  | Biberger             |
|                  |         |   | 2012/0063963 A1 | 3/2012  | Watanabe et al.      |
|                  |         |   | 2012/0097033 A1 | 4/2012  | Arnold et al.        |
|                  |         |   | 2012/0122660 A1 | 5/2012  | Andersen et al.      |
|                  |         |   | 2012/0124974 A1 | 5/2012  | Li et al.            |
|                  |         |   | 2012/0171098 A1 | 7/2012  | Hung et al.          |

(56)

## References Cited

## U.S. PATENT DOCUMENTS

2012/0214666 A1 8/2012 van den Hoek et al.  
 2012/0263633 A1 10/2012 Koplin et al.  
 2012/0285548 A1 11/2012 Layman et al.  
 2012/0308467 A1 12/2012 Carpenter et al.  
 2012/0313269 A1 12/2012 Kear et al.  
 2013/0034472 A1 2/2013 Cantrell et al.  
 2013/0064750 A1 3/2013 Zettl  
 2013/0079216 A1 3/2013 Biberger et al.  
 2013/0125970 A1 5/2013 Ko et al.  
 2013/0213018 A1 8/2013 Yin et al.  
 2013/0270355 A1 10/2013 Cotler et al.  
 2013/0280528 A1 10/2013 Biberger  
 2013/0281288 A1 10/2013 Biberger et al.  
 2013/0294989 A1 11/2013 Koch et al.  
 2013/0316896 A1 11/2013 Biberger  
 2013/0331257 A1 12/2013 Barcikowski et al.  
 2013/0345047 A1 12/2013 Biberger et al.  
 2014/0018230 A1 1/2014 Yin et al.  
 2014/0120355 A1 5/2014 Biberger  
 2014/0128245 A1 5/2014 Yin et al.  
 2014/0140909 A1 5/2014 Qi et al.  
 2014/0148331 A1 5/2014 Biberger et al.  
 2014/0161693 A1 6/2014 Brown et al.  
 2014/0209451 A1 7/2014 Biberger et al.  
 2014/0228201 A1 8/2014 Mendoza Gómez et al.  
 2014/0243187 A1 8/2014 Yin et al.  
 2014/0249021 A1 9/2014 van den Hoek et al.  
 2014/0252270 A1 9/2014 Lehman, Jr.  
 2014/0263190 A1 9/2014 Biberger et al.  
 2014/0318318 A1 10/2014 Layman et al.  
 2014/0338519 A1 11/2014 Biberger  
 2015/0093312 A1 4/2015 Yin et al.  
 2015/0140317 A1 5/2015 Biberger et al.  
 2015/0165418 A1 6/2015 Kearn et al.  
 2015/0165434 A1 6/2015 Yin et al.  
 2015/0196884 A1 7/2015 Layman  
 2015/0217229 A1 8/2015 Yin et al.  
 2015/0266002 A1 9/2015 Biberger et al.  
 2015/0314260 A1 11/2015 Biberger  
 2015/0314581 A1 11/2015 Biberger

## FOREIGN PATENT DOCUMENTS

CN 101301610 A 11/2008  
 DE 34 45 273 A1 6/1986  
 EP 0 347 386 A1 12/1989  
 EP 0 385 742 A1 9/1990  
 EP 1 134 302 A1 9/2001  
 EP 1 256 378 A2 11/2002  
 EP 1 619 168 A1 1/2006  
 EP 1 721 690 A1 11/2006  
 EP 1 790 612 A1 5/2007  
 EP 1 955 765 A1 8/2008  
 GB 1 307 941 A 2/1973  
 JP 30-13577 U 9/1955  
 JP 47-21256 U 2/1971  
 JP 49-31571 A 3/1974  
 JP 51-7582 U 7/1974  
 JP 52-165360 U 6/1976  
 JP 56-146804 A 11/1981  
 JP 58-160794 A 9/1983  
 JP 59-59410 A 4/1984  
 JP 61-086815 A 5/1986  
 JP 61-242644 A 10/1986  
 JP 62-102827 A 5/1987  
 JP 63-214342 A 9/1988  
 JP 1-164795 A 6/1989  
 JP 1-275708 A 11/1989  
 JP 2-6339 A 1/1990  
 JP 2-160040 A 6/1990  
 JP 2-203932 A 8/1990  
 JP 3-226509 A 10/1991  
 JP 5-193909 A 8/1993  
 JP 05-228361 A 9/1993

JP 05-324094 A 12/1993  
 JP 6-91162 A 4/1994  
 JP 6-93309 A 4/1994  
 JP 6-135797 A 5/1994  
 JP 6-172820 A 6/1994  
 JP 6-272012 A 9/1994  
 JP H6-065772 U 9/1994  
 JP 07-031873 A 2/1995  
 JP 7-20553 B2 3/1995  
 JP 7-120176 A 5/1995  
 JP 7-138020 A 5/1995  
 JP 7-207381 A 8/1995  
 JP 07-256116 A 10/1995  
 JP 8-158033 A 6/1996  
 JP 8-215576 A 8/1996  
 JP 8-217420 A 8/1996  
 JP 9-141087 A 6/1997  
 JP 10-130810 A 5/1998  
 JP 10-249198 A 9/1998  
 JP 11-502760 A 3/1999  
 JP 11-300198 A 11/1999  
 JP 2000-220978 A 8/2000  
 JP 2002-88486 A 3/2002  
 JP 2002-241812 A 8/2002  
 JP 2002-263496 A 9/2002  
 JP 2002-336688 A 11/2002  
 JP 2003-126694 A 5/2003  
 JP 2003-261323 A 9/2003  
 JP 2004-233007 A 8/2004  
 JP 2004-249206 A 9/2004  
 JP 2004-290730 A 10/2004  
 JP 2005-503250 A 2/2005  
 JP 2005-122621 A 5/2005  
 JP 2005-218937 A 8/2005  
 JP 2005-342615 A 12/2005  
 JP 2006-001779 A 1/2006  
 JP 2006-508885 A 3/2006  
 JP 2006-87965 A 4/2006  
 JP 2006-247446 A 9/2006  
 JP 2006-260385 A 9/2006  
 JP 2006-272265 A 10/2006  
 JP 2006-326554 A 12/2006  
 JP 2007-29859 A 2/2007  
 JP 2007-44585 A 2/2007  
 JP 2007-46162 A 2/2007  
 JP 2007-138287 A 6/2007  
 JP 2007-203129 A 8/2007  
 SU 493241 A 3/1976  
 TW 200611449 4/2006  
 TW 201023207 6/2010  
 WO WO-96/28577 A1 9/1996  
 WO WO-00/16882 3/2000  
 WO WO-00/72965 A1 12/2000  
 WO WO-02/092503 A1 11/2002  
 WO WO-03/094195 A1 11/2003  
 WO WO-2004/052778 A2 6/2004  
 WO WO-2005/063390 A1 7/2005  
 WO WO-2006/079213 A1 8/2006  
 WO WO-2006/096205 A2 9/2006  
 WO WO-2007/144447 A1 12/2007  
 WO WO-2008/088649 A1 7/2008  
 WO WO-2008/092478 A1 8/2008  
 WO WO-2008/130451 A2 10/2008  
 WO WO-2008/130451 A3 10/2008  
 WO WO-2009/017479 A1 2/2009  
 WO WO-2011/081833 A1 7/2011  
 WO WO-2011/081834 A1 7/2011  
 WO WO-2012/028695 A2 3/2012  
 WO WO-2013/028575 A1 2/2013  
 WO WO-2013/093597 A2 6/2013  
 WO WO-2013/151557 A1 10/2013

## OTHER PUBLICATIONS

Babin, A. et al. (1985). "Solvents Used in the Arts," *Center for Safety in the Arts*: 16 pages.

Bateman, J. E. et al. (Dec. 17, 1998). "Alkylation of Porous Silicon by Direct Reaction with Alkenes and Alkynes," *Angew. Chem Int. Ed.* 37(19):2683-2685.

(56)

## References Cited

## OTHER PUBLICATIONS

- Carrot, G. et al. (Sep. 17, 2002). "Surface-Initiated Ring-Opening Polymerization: A Versatile Method for Nanoparticle Ordering," *Macromolecules* 35(22):8400-8404.
- Chaim, R. et al. (2009). "Densification of Nanocrystalline  $Y_2O_3$  Ceramic Powder by Spark Plasma Sintering," *Journal of European Ceramic Society* 29: 91-98.
- Chau, J. K. H. et al. (2005). "Microwave Plasma Synthesis of Silver Nanopowders," *Materials Letters* 59: 905-908.
- Chen, H.-S. et al. (Jul. 3, 2001). "On the Photoluminescence of Si Nanoparticles," *Mater. Phys. Mech.* 4:62-66.
- Chen, W.-J. et al. (Mar. 18, 2008). "Functional  $Fe_3O_4/TiO_2$  Core/Shell Magnetic Nanoparticles as Photokilling Agents for Pathogenic Bacteria," *Small* 4(4): 485-491.
- Das, N. et al. (2001). "Influence of the Metal Function in the "One-Pot" Synthesis of 4-Methyl-2-Pentanone (Methyl Isobutyl Ketone) from Acetone Over Palladium Supported on  $Mg(Al)O$  Mixed Oxides Catalysts," *Catalysis Letters* 71(3-4): 181-185.
- Faber, K. T. et al. (Sep. 1988). "Toughening by Stress-Induced Microcracking in Two-Phase Ceramics," *Journal of the American Ceramic Society* 71: C-399-C401.
- Fauchais, P. et al. (Jun. 1989). "La Projection Par Plasma: Une Revue," *Ann. Phys. Fr.* 14(3):261-310.
- Fauchais, P. et al. (Jan. 1993). "Les Dépôts Par Plasma Thermique," *Revue Générale De L'Electricité*, RGE, Paris, France, No. 2, pp. 7-12 (in French).
- Fauchais, P. et al. (Jan. 1996). "Plasma Spray: Study of the Coating Generation," *Ceramics International* 22(4):295-303.
- Fojtik, A. et al. (Apr. 29, 1994). "Luminescent Colloidal Silicon Particles," *Chemical Physics Letters* 221:363-367.
- Fojtik, A. (Jan. 13, 2006). "Surface Chemistry of Luminescent Colloidal Silicon Nanoparticles," *J. Phys. Chem. B.* 110(5):1994-1998.
- Gangeri, M. et al. (2009). "Fe and Pt Carbon Nanotubes for the Electrocatalytic Conversion of Carbon Dioxide to Oxygenates," *Catalysis Today* 143: 57-63.
- Gutsch, A. et al. (2002). "Gas-Phase Production of Nanoparticles," *Kona* No. 20, pp. 24-37.
- Han, B. Q. et al. (Jan. 2004). "Deformation Mechanisms and Ductility of Nanostructured Al Alloys," *Mat. Res. Soc. Symp. Proc.* 821:p. 9.1.1-p. 9.1.6.
- Heberlein, J. (2002). "New Approaches in Thermal Plasma Technology," *Pure Appl. Chem.* 74(3):327-335.
- Hua, F. et al. (Mar. 2006). "Organically Capped Silicon Nanoparticles With Blue Photoluminescence Prepared by Hydrosilylation Followed by Oxidation," *Langmuir* 22(9):4363-4370.
- Ihle, G. et al. (1998). "Ordered Porous Materials as Media for the Organization of Matter on the Nanoscale," *Applied Organometallic Chemistry* 12: 305-314.
- Ji, Y. et al. (Nov. 2002). "Processing and Mechanical Properties of  $Al_2O_3$ -5 vol.% Cr Nanocomposites," *Journal of the European Ceramic Society* 22(12):1927-1936.
- Jouet, R. J. et al. (Jan. 25, 2005). "Surface Passivation of Bare Aluminum Nanoparticles Using Perfluoroalkyl Carboxylic Acids," *Chem. Mater.* 17(11):2987-2996.
- Kenvin, J. C. et al. (1992). "Supported Catalysts Prepared from Mononuclear Copper Complexes: Catalytic Properties," *J. Catalysis* 135:81-91.
- Konrad, H. et al. (1996). "Nanostructured Cu—Bi Alloys Prepared by Co-Evaporation in a Continuous Gas Flow," *Nanostructured Materials* 7(6):605-610.
- Kim, N. Y. et al. (Mar. 5, 1997). "Thermal Derivatization of Porous Silicon with Alcohols," *J. Am. Chem. Soc.* 119(9):2297-2298.
- Kwon, Y.-S. et al. (Apr. 30, 2003). "Passivation Process for Superfine Aluminum Powders Obtained by Electrical Explosion of Wires," *Applied Surface Science* 211:57-67.
- Lakis, R. E. et al. (1995). "Alumina-Supported Pt—Rh Catalysts: I. Microstructural Characterization," *Journal of Catalysis* 154: 261-275.
- Langner, A. et al. (Aug. 25, 2005). "Controlled Silicon Surface Functionalization by Alkene Hydrosilylation," *J. Am. Chem. Soc.* 127(37):12798-12799.
- Li, D. et al. (Apr. 9, 2005). "Environmentally Responsive "Hairy" Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques," *J. Am. Chem. Soc.* 127(7):6248-6256.
- Li, X. et al. (May 25, 2004). "Surface Functionalization of Silicon Nanoparticles Produced by Laser-Driven Pyrolysis of Silane Followed by  $HF-HNO_3$  Etching," *Langmuir* 20(11):4720-4727.
- Liao, Y.-C. et al. (Jun. 27, 2006). "Self-Assembly of Organic Monolayers on Aerosolized Silicon Nanoparticles," *J. Am. Chem. Soc.* 128(28):9061-9065.
- Liu, S.-M. et al. (Jan. 13, 2006). "Enhanced Photoluminescence from Si Nano-Organosols by Functionalization With Alkenes and Their Size Evolution," *Chem. Mater.* 18(3):637-642.
- Luo, J. et al. (2008). "Core/Shell Nanoparticles as Electrocatalysts for Fuel Cell Reactions," *Advanced Materials* 20: 4342-4347.
- Mignard, D. et al. (2003). "Methanol Synthesis from Flue-Gas  $CO_2$  and Renewable Electricity: A Feasibility Study," *International Journal of Hydrogen Energy* 28: 455-464.
- Mühlenweg, H. et al. (2004). "Gas-Phase Reactions—Open Up New Roads to Nanoproducts," *Degussa ScienceNewsletter* No. 08, pp. 12-16.
- Nagai, Y. et al. (Jul. 3, 2006). "Sintering Inhibition Mechanism of Platinum Supported on Ceria-Based Oxide and Pt-Oxide-Support Interaction," *J. Catalysis* 242:103-109.
- NASA (2009). "Enthalpy," Article located at <http://www.grc.nasa.gov/WWW/K-12/airplane/enthalpy.html>, published by National Aeronautics and Space Administration on Nov. 23, 2009, 1 page.
- Neiner, D. (Aug. 5, 2006). "Low-Temperature Solution Route to Macroscopic Amounts of Hydrogen Terminated Silicon Nanoparticles," *J. Am. Chem. Soc.* 128:11016-11017.
- Netzer, L. et al. (1983). "A New Approach to Construction of Artificial Monolayer Assemblies," *J. Am. Chem. Soc.* 105(3):674-676.
- Park, H.-Y. et al. (May 30, 2007). "Fabrication of Magnetic Core@Shell Fe Oxide@Au Nanoparticles for Interfacial Bioactivity and Bio-Separation," *Langmuir* 23: 9050-9056.
- Park, N.-G. et al. (Feb. 17, 2004). "Morphological and Photoelectrochemical Characterization of Core-Shell Nanoparticle Films for Dye-Sensitized Solar Cells: Zn—O Type Shell on  $SnO_2$  and  $TiO_2$  Cores," *Langmuir* 20: 4246-4253.
- "Plasma Spray and Wire Flame Spray Product Group," located at <http://www.processmaterials.com/spray.html>, published by Process Materials, Inc., last accessed Aug. 5, 2013, 2 pages.
- "Platinum Group Metals: Annual Review 1996" (Oct. 1997). Engineering and Mining Journal, p. 63.
- Rahaman, R. A. et al. (1995). "Synthesis of Powders," in *Ceramic Processing and Sintering*. Marcel Dekker, Inc., New York, pp. 71-77.
- Sailor, M. J. (1997). "Surface Chemistry of Luminescent Silicon Nanocrystallites," *Adv. Mater.* 9(10):783-793.
- Schimpf, S. et al. (2002). "Supported Gold Nanoparticles: In-Depth Catalyst Characterization and Application in Hydrogenation and Oxidation Reactions," *Catalysis Today* 2592: 1-16.
- Stiles, A. B. (Jan. 1, 1987). "Manufacture of Carbon-Supported Metal Catalysts," in *Catalyst Supports and Supported Catalysts*, Butterworth Publishers, MA, pp. 125-132.
- Subramanian, S. et al. (1991). "Structure and Activity of Composite Oxide Supported Platinum—Iridium Catalysts," *Applied Catalysts* 74: 65-81.
- Tao, Y.-T. (May 1993). "Structural Comparison of Self-Assembled Monolayers of *n*-Alkanoic Acids on the surfaces of Silver, Copper, and Aluminum," *J. Am. Chem. Soc.* 115(10):4350-4358.
- Ünal, N. et al. (Nov. 2011). "Influence of WC Particles on the Microstructural and Mechanical Properties of 3 mol%  $Y_2O_3$  Stabilized  $ZrO_2$  Matrix Composites Produced by Hot Pressing," *Journal of the European Ceramic Society* (31)13: 2267-2275.
- Vardelle, A. et al. (1996). "Coating Generation: Vaporization of Particles in Plasma Spraying and Splat Formation," Université de Limoges, 123 Avenue A. Thomas 87000, Limoges, France, *Pure & Appl. Chem.* 68(5):1093-1099.

(56)

**References Cited****OTHER PUBLICATIONS**

Vardelle, M. et al. (Jun. 1991). "Experimental Investigation of Powder Vaporization in Thermal Plasma Jets," *Plasma Chemistry and Plasma Processing* 11(2):185-201.

Viswanathan, V. et al. (2006). "Challenges and Advances in Nanocomposite Processing Techniques," *Materials Science and Engineering R* 54: 121-285.

Wan, J. et al. (2005). "Spark Plasma Sintering of Silicon Nitride/Silicon Carbide Nanocomposites with Reduced Additive Amounts," *Scripta Materialia* 53: 663-667.

Yoshida, T. (1994). "The Future of Thermal Plasma Processing for Coating," *Pure & Appl. Chem.* 66(6):1223-1230.

Zou, J. et al. (Jun. 4, 2004). "Solution Synthesis of Ultrastable Luminescent Siloxane-Coated Silicon Nanoparticles," *Nano Letters* 4(7):1181-1186.

International Search Report mailed on Feb. 3, 2011, for PCT Patent Application No. PCT/US2010/059760, filed Dec. 9, 2010, published on Jun. 23, 2011, as WO 2011/75399, 1 page.

Written Opinion mailed on Feb. 3, 2011, for PCT Patent Application No. PCT/US2010/059760, filed Dec. 9, 2010, published on Jun. 23, 2011, as WO 2011/75399, 13 pages.

U.S. Appl. No. 13/291,983, filed Nov. 8, 2011, for Layman et al.

U.S. Appl. No. 12/152,084, filed May 9, 2008, for Biberger.

U.S. Appl. No. 13/028,693, filed Feb. 16, 2011, for Biberger.

U.S. Appl. No. 12/943,909, filed Nov. 10, 2010, for Layman.

U.S. Appl. No. 12/152,111, filed May 9, 2008, for Biberger et al.

U.S. Appl. No. 12/151,830, filed May 8, 2008, for Biberger et al.

U.S. Appl. No. 12/968,248, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/968,245, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/968,241, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/968,239, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/969,128, filed Dec. 15, 2010, for Biberger.

U.S. Appl. No. 12/962,463, filed Dec. 7, 2010, for Leamon.

U.S. Appl. No. 12/961,030, filed Dec. 6, 2010, for Lehman.

U.S. Appl. No. 12/961,108, filed Dec. 6, 2010, for Lehman.

U.S. Appl. No. 12/961,200, filed Dec. 6, 2010, for Lehman.

U.S. Appl. No. 12/968,253, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/968,235, filed Dec. 14, 2010, for Biberger.

U.S. Appl. No. 12/969,306, filed Dec. 15, 2010, for Lehman et al.

U.S. Appl. No. 12/969,447, filed Dec. 15, 2010, for Biberger et al.

U.S. Appl. No. 12/969,087, filed Dec. 15, 2010, for Biberger.

U.S. Appl. No. 12/962,533, filed Dec. 7, 2010, for Yin et al.

U.S. Appl. No. 12/962,523, filed Dec. 7, 2010, for Yin et al.

U.S. Appl. No. 12/001,643, filed Dec. 11, 2007, for Biberger et al.

U.S. Appl. No. 12/474,081, filed May 28, 2009, for Biberger et al.

U.S. Appl. No. 12/001,602, filed Dec. 11, 2007, for Biberger et al.

U.S. Appl. No. 12/001,644, filed Dec. 11, 2007, for Biberger et al.

U.S. Appl. No. 12/969,457, filed Nov. 15, 2010, for Leamon et al.

U.S. Appl. No. 12/969,503, filed Nov. 15, 2010, for Leamon et al.

U.S. Appl. No. 12/954,813, filed Nov. 26, 2010, for Biberger.

U.S. Appl. No. 12/954,822, filed Nov. 26, 2010, for Biberger.

Büchel, R. et al. (2009). "Influence of Pt Location on BaCO<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> During NO Storage Reduction," *Journal of Catalysis* 261: 201-207.

Date, A. R. et al. (1987). "The Potential of Fire Assay and Inductively Coupled Plasma Source Mass Spectrometry for the Determination of Platinum Group Elements in Geological Materials," *Analyst* 112: 1217-1222.

Lamoureux, E. et al. (2007). "Identification of Key Parameters for the Selective Growth of Single or Double Wall Carbon Nanotubes on FeMo/Al<sub>2</sub>O<sub>3</sub> CVD Catalysts," *Applied Catalysts A: General* 323: 162-173.

Martinez-Hansen, V. et al. (2009). "Development of Aligned Carbon Nanotubes Layers Over Stainless Steel Mesh Monoliths," *Catalysis Today* 1475: 571-575.

Panchula, M. L. et al. (2003). "Nanocrystalline Aluminum Nitride: I, Vapor-Phase Synthesis in a Forced-Flow Reactor," *Journal of the American Ceramic Society* 86(7): 1114-1120.

Strobel, R. et al. (2003). "Flame-made Platinum/Alumina: Structural Properties and Catalytic Behaviour in Enantioselective Hydrogenation," *Journal of Catalysis* 213: 296-304.

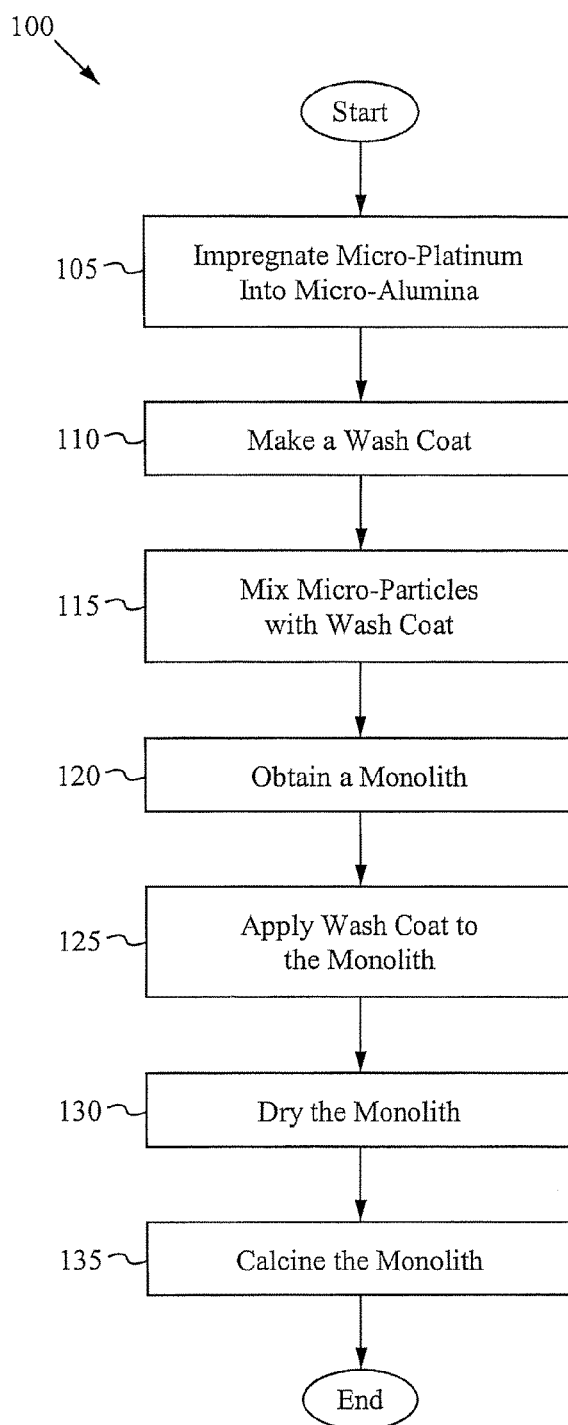
Birlik, I. et al. (Jun. 15, 2010). "Nanoparticle Doped YBCO Films Prepared by Chemical Solution Deposition Method," *6th Nanoscience and Nanotechnology Conference*, Izmir, Turkey: 1 page.

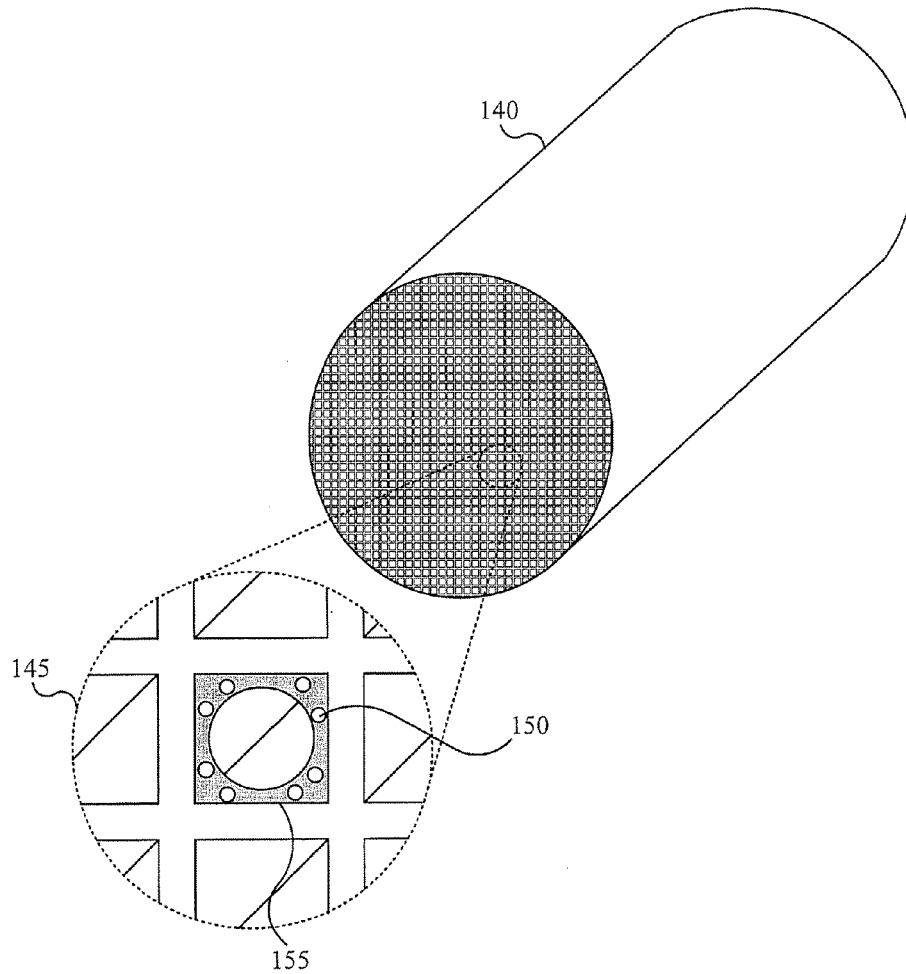
COSPHERIC LLC. (Mar. 13, 2010). "Porous Ceramics: Application for Polyethylene Microspheres," Microspheres Online, located at <http://microspheres.us/microsphere-manufacturing/porous-ceramics-polyethylene-microspheres/177.html>, last accessed Mar. 17, 2015, 6 pages.

Jensen, J. et al. (2000). "Preparation of ZnO—Al<sub>2</sub>O<sub>3</sub> Particles in a Premixed Flame," *Journal of Nanoparticle Research* 2: 363-373.

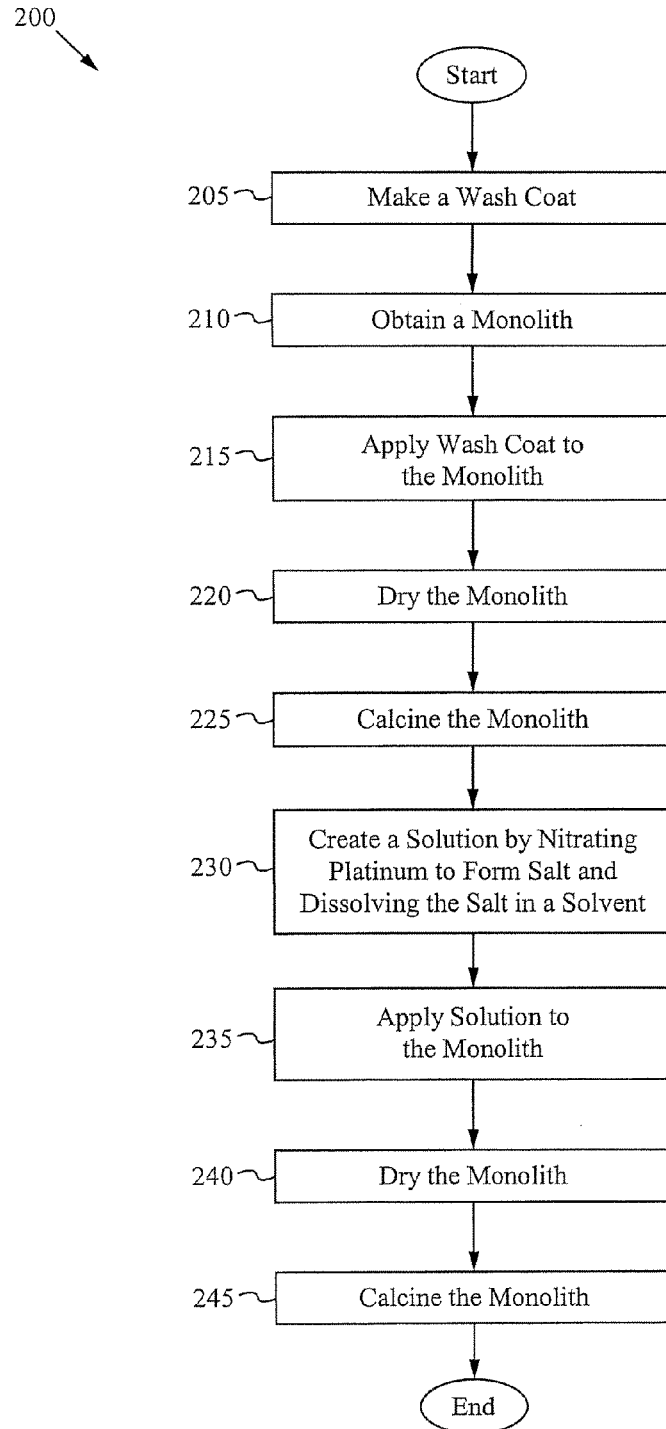
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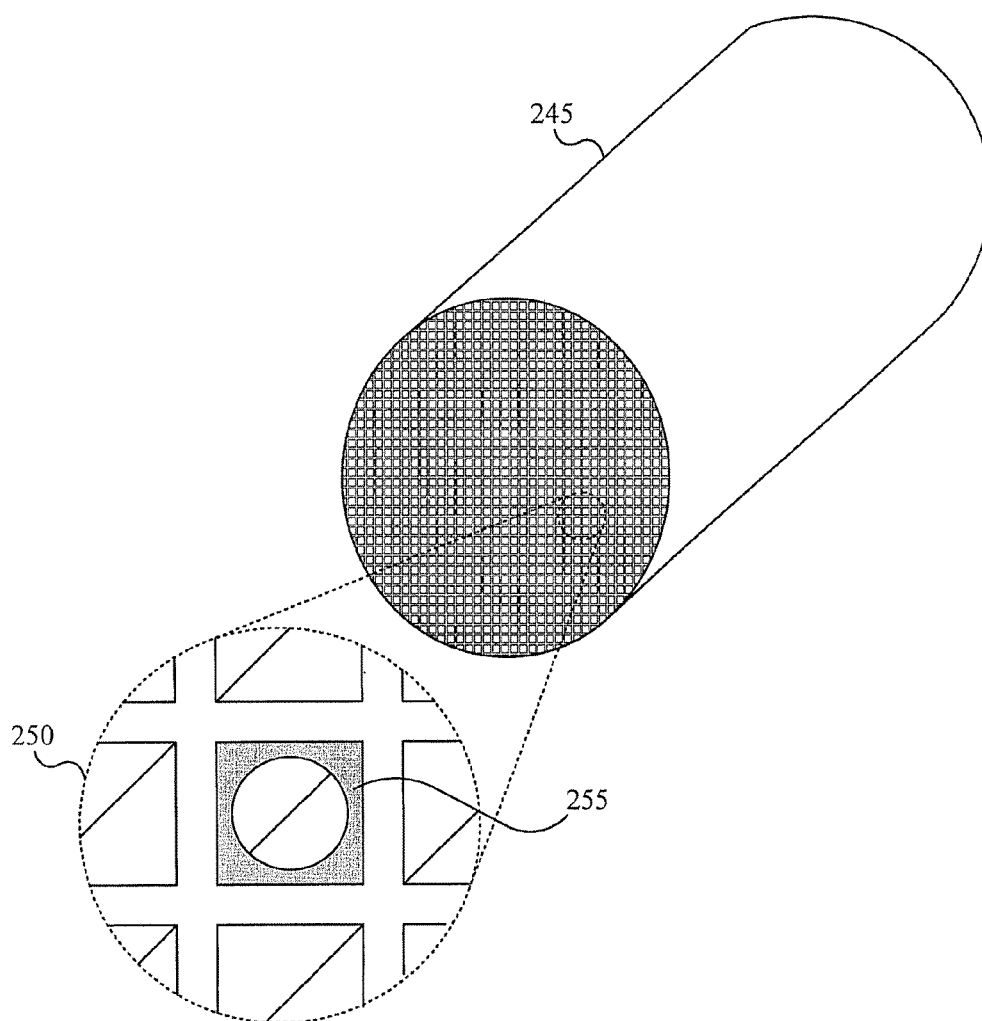


**Fig. 1A (Prior Art)**

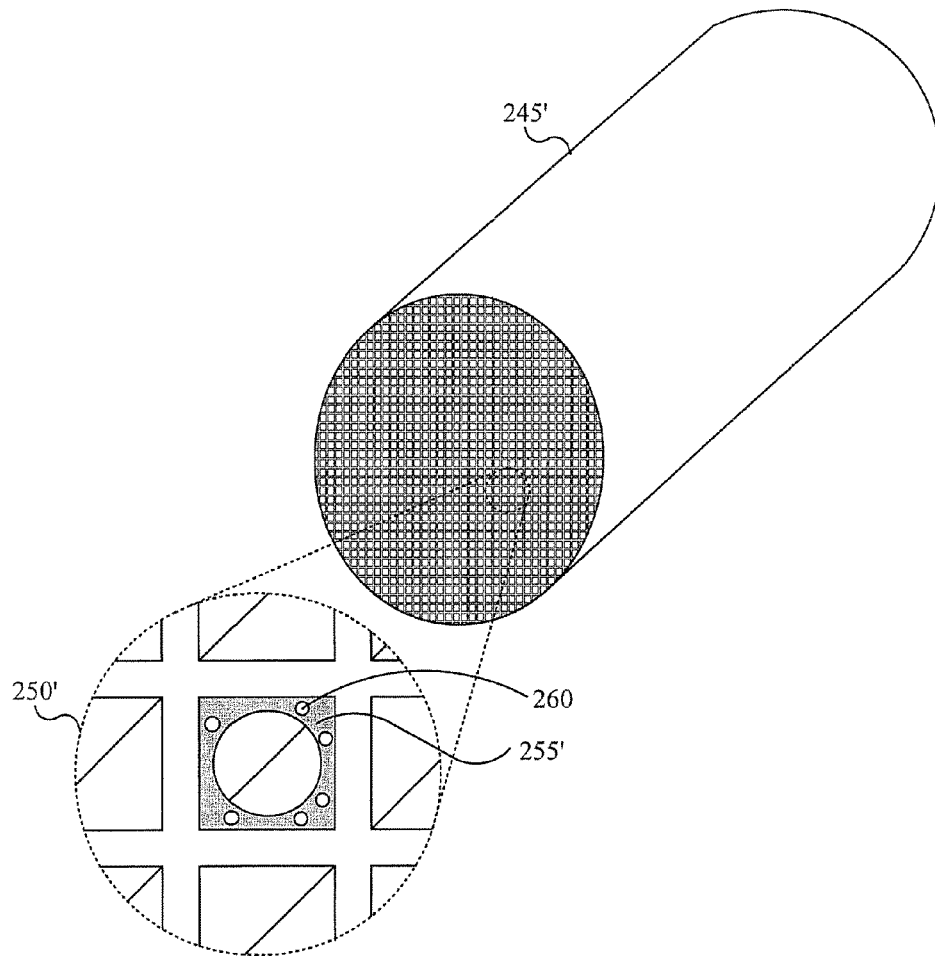


**Fig. 1B (Prior Art)**

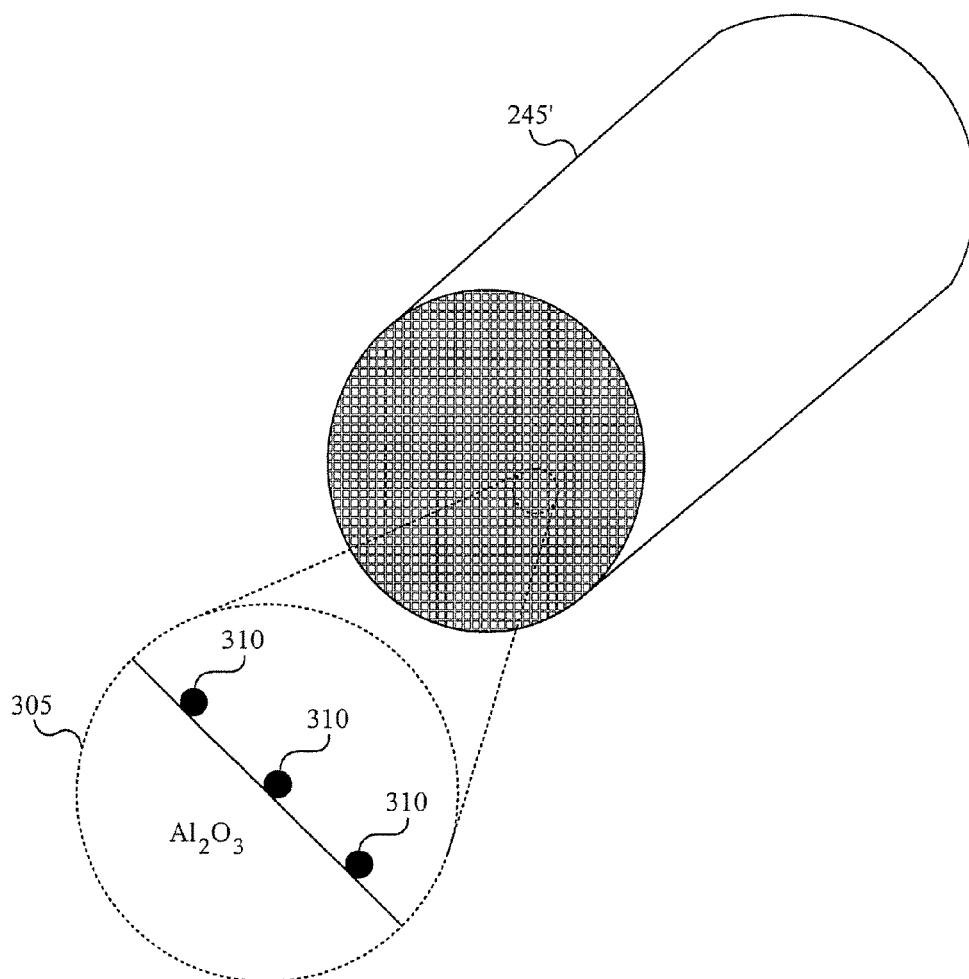
**Fig. 2A (Prior Art)**

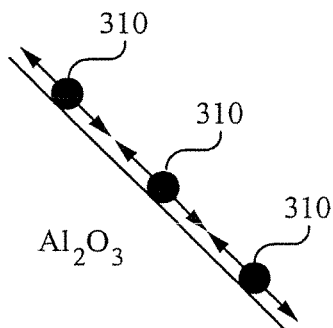


**Fig. 2B (Prior Art)**

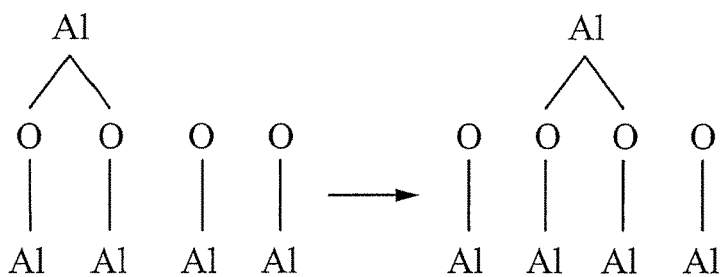


**Fig. 2C (Prior Art)**

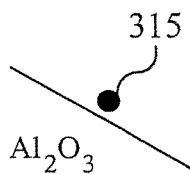
**Fig. 3A**



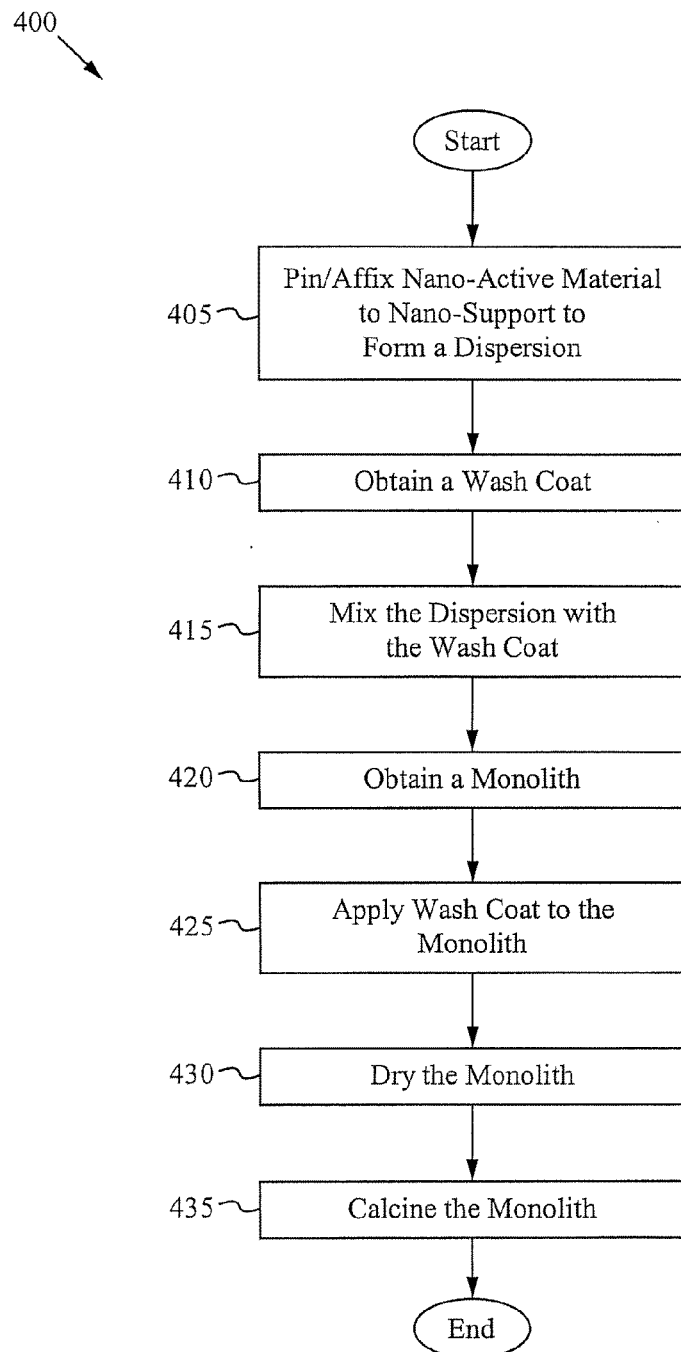
**Fig. 3B**



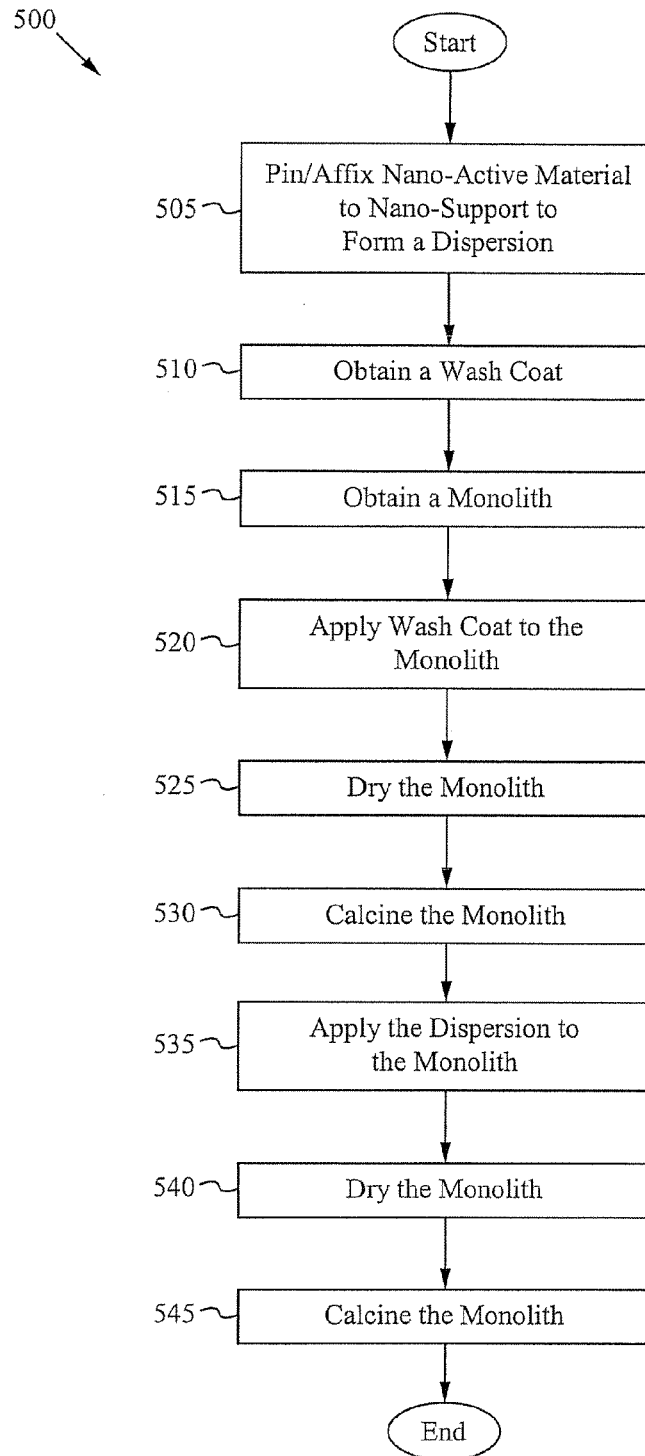
**Fig. 3C**

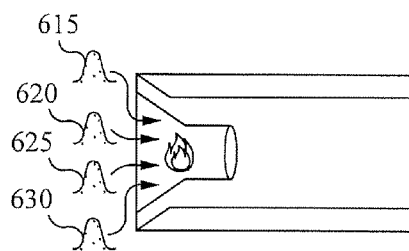


**Fig. 3D**

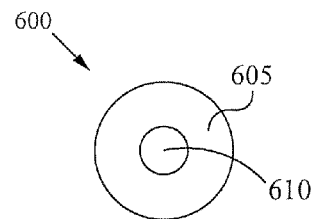
**Fig. 4**



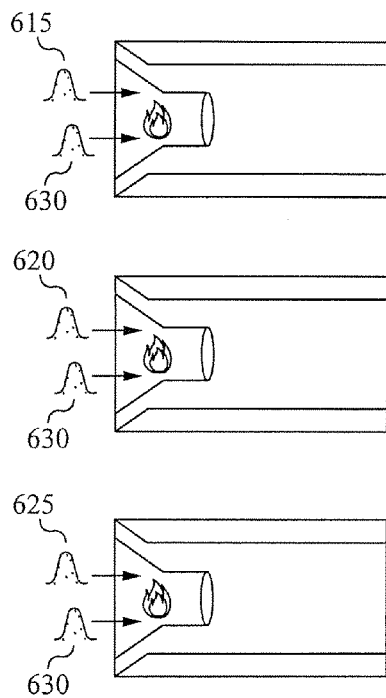
**Fig. 5**



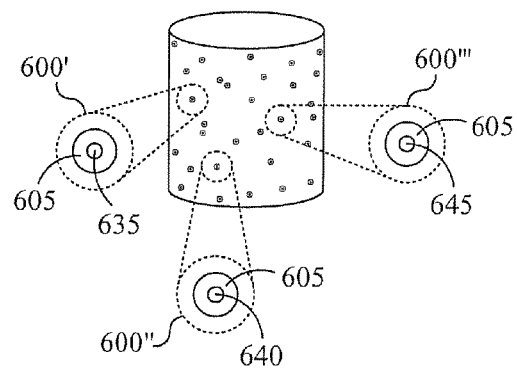
**Fig. 6A**



**Fig. 6B**



**Fig. 7A**



**Fig. 7B**

# ADVANCED CATALYSTS FOR AUTOMOTIVE APPLICATIONS

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 12/962,490, filed Dec. 7, 2010 which claims priority to U.S. Provisional Patent Application Ser. No. 61/284,329, filed Dec. 15, 2009 and entitled "MATERIALS PROCESSING," which are hereby incorporated herein by reference in their entirety as if set forth herein.

## BACKGROUND OF THE INVENTION

A catalytic converter for a car uses a catalyst to convert, for example, three harmful compounds in car exhaust into less harmful compounds. The three harmful compounds include hydrocarbons in the form of unburned gasoline, carbon monoxide formed by the combustion of gasoline, and nitrogen oxide created when heat in the engine forces nitrogen in the air to combine with oxygen. There are two main structures used in catalytic converters—honeycomb and ceramic beads. Most automobiles today use the honeycomb structure. The honeycomb structure is housed in a muffler-like package that comes before the exhaust pipe. The catalyst helps to convert carbon monoxide into carbon dioxide, the hydrocarbons into carbon dioxide and water, and the nitrogen oxides back into nitrogen and oxygen.

Various methods of manufacturing the catalyst used in the catalytic converter exist in the art. FIG. 1A illustrates a first conventional method of manufacturing the catalyst. The first method is known as a one-dip process. At a step 105, micron-sized platinum (Pt) ions are impregnated into micron-sized alumina ( $\text{Al}_2\text{O}_3$ ) ions, resulting in micro-particles. The micro-particles have platinum atoms on the alumina ions. At a step 110, a wash coat is made using micron-sized oxides that include pint size alumina and pint size silica ( $\text{SiO}_2$ ), a certain amount of stabilizers for the alumina, and a certain amount of promoters. At a step 115, the micro-particles are mixed together with the wash coat. At a step 120, a cylindrical-shaped ceramic monolith is obtained. A cross-section of the monolith contains 300-600 channels per square inch. The channels are linear square channels that run from the front to the back of the monolith. At a step 125, the monolith is coated with the wash coat. This can be achieved by dipping the monolith in the wash coat. As such, the channels of the monolith are coated with a layer of wash coat. At a step 130, the monolith is dried. The layer of wash coat has an irregular surface, which has a far greater surface area than a flat surface. In addition, the wash coat when dried is a porous structure. The irregular surface and the porous structure are desirable because they give a high surface area, approximately 100-250  $\text{m}^2/\text{g}$ , and thus more places for the micro-particles to bond thereto. As the monolith dries, the micro-particles settle on the surface and pores of the monolith. At a step 135, the monolith is calcined. The calcination bonds the components of the wash coat to the monolith by oxide to oxide coupling. The catalyst is formed. FIG. 1B illustrates a microscopic view 145 of a channel of the monolith 140 that is coated with the layer of wash coat 150 having platinum atoms 155.

FIG. 2A illustrates a second conventional method of manufacturing the catalyst. The second method is known as a two-dip process. At a step 205, a wash coat is made using micron-sized oxides that include pint size alumina and pint size silica, a certain amount of stabilizers for the alumina, and a certain amount of promoters. At a step 210, a cylindrical-

shaped ceramic monolith is obtained. At a step 215, the monolith is coated with the wash coat such as via dipping. As such, the channels are also coated with a layer of wash coat. Typically, the layer of wash coat has an irregular surface which has a far greater surface area than a flat surface. FIG. 2B illustrates a microscopic view 250 of a channel of the monolith 245 coated with the layer of the wash coat 255. Returning to FIG. 2A, at a step 220, the monolith is dried. The wash coat when dried is a porous structure. At a step 225, the monolith is calcined. The calcination bonds the components of the wash coat to the monolith by oxide to oxide coupling. Micron-sized alumina oxides are then impregnated with micron-sized platinum ions and other promoters using a method that is well known in the art. Specifically, at a step 230, platinum is nitrated, forming salt ( $\text{PtNO}_3$ ). The  $\text{PtNO}_3$  is dissolved in a solvent such as water, thereby creating a dispersion. At step 235, the monolith is dipped into the solution. At a step 240, the monolith is dried. At a step 245, the monolith is calcined. The catalyst is formed. FIG. 2C illustrates another microscopic view 250' of the channel of the monolith 245' coated with the layer of wash coat 255' having platinum atoms 260.

FIG. 3A illustrates a microscopic view 305 of a surface of the layer of the wash coat after calcination. Platinum atoms 310 are attached to oxygen atoms of the alumina. When exhaust gas goes through the catalytic converter, the platinum atoms 310 help reduce the harmful compounds by converting them into less harmful compounds. However, these various methods of manufacturing the catalyst used in the catalytic converter suffer from a number of shortcomings. For example, the platinum atoms 310 are not fixed to their bonded oxygen atoms of the alumina and are able to move around to other available oxygen atoms as illustrated in FIGS. 3B-3C. As the platinum atoms 310 move, the platinum atoms 310 begin to coalesce with other platinum atoms resulting in larger particles 315, as shown in FIG. 3D, and a more energetically favorable state. It is understood that as the platinum particles become larger, it detrimentally affects the catalyst since surface area of the platinum atoms decreases. In high temperature applications, such as in an aged catalytic converting testing, the movement of platinum atoms is magnified. In addition, since cost of platinum is extremely expensive, excessive use of platinum is unwanted.

The present invention addresses at least these limitations in the prior art.

## SUMMARY OF THE INVENTION

In one aspect, a catalytic converter includes a honeycomb structure with an at least one nano-particle on the honeycomb structure. In some embodiments, the at least one nano-particle includes nano-active material and nano-support. The nano-active material is typically on the nano-support. The nano-active material is platinum, palladium, rhodium, or an alloy. The alloy is of platinum, palladium, and rhodium. The nano-support is alumina. In other embodiments, the nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

In another aspect, a cordierite substrate in a catalytic converter includes a first type of nano-particles, a second type of nano-particles, and a third type of nano-particles. In some embodiments, the first type of nano-particles includes nano-active material and nano-support. The nano-active material is platinum and the nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support. In other embodiments, the second type of

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nano-particles comprises nano-active material and nano-support. The nano-active material is palladium and the nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support. In other embodiments, the third type of nano-particles comprises nano-active material and nano-support. The nano-active material is rhodium and the nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

Yet, in another aspect, a method of making a catalytic converter includes creating a dispersion using an at least one nano-particle and obtaining a wash coat. In some embodiments, the at least one nano-particle includes nano-active material and nano-support. The nano-active material is platinum, palladium, rhodium, or an alloy. The nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support. In other embodiments, the creating step comprises mixing a carrier material and different catalyst materials in a high temperature condensation technology, thereby producing the at least one nano-particle, and combining it with a liquid. The carrier material is alumina. The different catalyst materials include platinum, palladium, and rhodium. Typically, the high temperature condensation technology is plasma. Alternatively, the creating step comprises mixing a carrier material and a first catalyst material in a high temperature condensation technology, thereby producing a first type of nano-particles, mixing the carrier material and a second catalyst material in the high temperature condensation technology, thereby producing a second type of nano-particles, mixing the carrier material and a third catalyst material in the high temperature condensation technology, thereby producing a third type of nano-particles, collecting together the first type of nano-particles, the second type of nano-particles, and a third type of nano-particles, and combining with a liquid. The carrier material is alumina. The first catalyst material is platinum. The second catalyst material is palladium. The third catalyst material is rhodium.

Yet, in other embodiments, the method of making a catalytic converter further includes mixing the dispersion with the wash coat, applying the mix to a monolith, drying the monolith, and calcining the monolith. Alternatively, the method of making a catalytic converter further includes applying the wash coat to a monolith, drying the monolith, calcining the monolith, administering the dispersion to the monolith, drying the monolith, and calcining the monolith.

Yet, in another aspect, a method of making a three-way catalytic converter includes creating a dispersion by using different types of nano-particles, obtaining a wash coat, mixing the dispersion with the wash coat, applying the mix to a monolith, drying the monolith, and calcining the monolith. The creating step includes using a high temperature condensation technology. In some embodiments, the high temperature condensation technology is plasma. Each of the different types of nano-particles comprises nano-active material and nano-support. The nano-active material is platinum, palladium, rhodium, or an alloy. The nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

Yet, in another aspect, a method of making a three-way catalytic converter includes creating a dispersion using different types of nano-particles, obtaining a wash coat, applying the wash coat to a monolith, drying the monolith, calcining the monolith, administering the dispersion to the

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monolith, drying the monolith, and calcining the monolith. The creating step includes using a high temperature condensation technology. In some embodiments, the high temperature condensation technology is plasma. Each of the different types of nano-particles includes nano-active material and nano-support. The nano-active material is platinum, palladium, rhodium, or an alloy. The nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

Yet, in another aspect, a method of making a two-way catalytic converter includes creating a dispersion by using same type of nano-particles, obtaining a wash coat, mixing the dispersion with the wash coat, applying the mix to a monolith, drying the monolith, and calcining the monolith. The creating step includes using a high temperature condensation technology. In some embodiments, the high temperature condensation technology is plasma. Each of the same type of nano-particles includes nano-active material and nano-support. The nano-active material is platinum. The nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

Yet, in another aspect, a method of making a two-way catalytic converter includes creating a dispersion using same type of nano-particles, obtaining a wash coat, applying the wash coat to a monolith, drying the monolith, calcining the monolith, administering the dispersion to the monolith, drying the monolith, and calcining the monolith. The creating step includes using a high temperature condensation technology. In some embodiments, the high temperature condensation technology is plasma. Each of the same type of nano-particles includes nano-active material and nano-support. The nano-active material is platinum. The nano-support is alumina. The nano-support includes a partially reduced alumina surface, which limits movement of the nano-active material on a surface of the nano-support.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A-1B illustrate a first conventional method of manufacturing a catalyst.

FIGS. 2A-2C illustrate a second conventional method of manufacturing the catalyst.

FIGS. 3A-3C illustrate activity on a surface of a layer of wash coat on the monolith using the first conventional method and the second conventional method.

FIG. 3D illustrates platinum atoms coalesced into a large particle.

FIG. 4 illustrates a first inventive process of creating an advanced catalyst in accordance with the present invention.

FIG. 5 illustrates a first inventive process of creating an advanced catalyst in accordance with the present invention.

FIG. 6A illustrates a first method of creating a dispersion in accordance with the present invention.

FIG. 6B illustrates a nano-particle in accordance with the present invention.

FIG. 7A illustrates a second method of creating a dispersion in accordance with the present invention.

FIG. 7B illustrates a collection of different nano-particles in accordance with the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to implementations of the present invention as illustrated in the accompanying drawings. The drawings may not be to scale. The same refer-

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ence indicators will be used throughout the drawings and the following detailed description to refer to identical or like elements. In the interest of clarity, not all of the routine features of the implementations described herein are shown and described. It will, of course, be appreciated that in the development of any such actual implementation, numerous implementation-specific decisions must be made in order to achieve the developer's specific goals, such as compliance with application, safety regulations and business related constraints, and that these specific goals will vary from one implementation to another and from one developer to another. Moreover, it will be appreciated that such a development effort will be a routine undertaking of engineering for those of ordinary skill in the art having the benefit of this disclosure.

The following description of the invention is provided as an enabling teaching which includes the best currently known embodiment. One skilled in the relevant arts, including but not limited to chemistry, physics and material sciences, will recognize that many changes can be made to the embodiment described, while still obtaining the beneficial results of the present invention. It will also be apparent that some of the desired benefits of the present invention can be obtained by selecting some of the features of the present invention without utilizing other features. Accordingly, those who work in the art will recognize that many modifications and adaptations to the present inventions are possible and may even be desirable in certain circumstances, and are a part of the present invention. Thus, the following description is provided as illustrative of the principles of the present invention and not in limitation thereof, since the scope of the present invention is defined by the claims.

Harmful compounds from internal combustion engines include carbon monoxide (CO), hydrocarbons ( $H_aC_b$ ), and oxides of nitrogen ( $NO_x$ ). Two forms of internal combustion engines are diesel engines and gas engines. A catalytic converter is designed to reduce these harmful compounds by converting them into less harmful compounds. As discussed above, conventional catalysts used in catalytic converters use micro-particles such as micron-sized oxides and micron-sized catalyst materials (e.g. platinum). Embodiments of the present invention use nano-sized oxides and nano-sized catalyst materials to create advanced catalysts usable in catalytic converters of diesel engines and gas engines.

The term "nano-particle" is generally understood by those of ordinary skill to encompass a particle having a diameter in the order of nanometers, as described herein.

#### Diesel Engines

A diesel engine includes a diesel oxidation catalyst (DOC), a separate NO<sub>x</sub> reduction technology, and a diesel particulate filter (DPF). The DOC is a two-way catalytic converter, which converts (1) CO and O<sub>2</sub> to CO<sub>2</sub> and (2)  $H_aC_b$  and O<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O. The DOC uses platinum as an oxidizing agent. Conventional methods of creating the DOC use micron-size platinum ions. Embodiments of the present invention use nano-sized platinum particles instead. FIGS. 4-5 illustrate two inventive processes of creating an advanced DOC catalyst in accordance with the present invention. The separate NO<sub>x</sub> reduction technology reduces the NO<sub>x</sub> emissions by using urea as a reducing agent. The DPF catches subparticles (e.g. nongaseous hydrocarbons) from an exhaust gas of the diesel engine.

FIG. 4 illustrates a first inventive process 400 for creating the advanced DOC catalyst in accordance with the present invention. At a step 405, nano-active materials are pinned or affixed to nano-supports, forming nano-particles, by using a high temperature condensation technology such as a plasma gun. In some embodiments, the nano-active materials are

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gaseous platinum atoms, and the nano-supports are some form of alumina, such as aluminum plus oxygen. For the sake of brevity, platinum will be discussed herein, but it will be apparent to those of ordinary skill in the art that different platinum group metals can be used to take advantage of their different properties. Since nano-active materials are strongly attached to nano-supports, movement or coalescing/conglomeration of the nano-active materials is limited, prevented, or both. The nano-particles are then combined with a liquid to form a dispersion. The nano-particles and the dispersion are created using methods described in detail in U.S. patent application Ser. No. 12/001,643, filed Dec. 11, 2007, which is hereby incorporated by reference. At a step 410, a wash coat is obtained. The wash coat is commercially purchased or is made. Typically, the wash coat is a slurry. The wash coat is made by using micron-sized oxides that include alumina and silica. In some embodiments, a certain amount of stabilizers for the alumina and a certain amount of promoters are also added to the wash coat. Typically, there is no difference between the commercially purchased wash coat and the created wash coat. At a step 415, the dispersion is mixed with the wash coat. At a step 420, a cylindrical-shaped ceramic monolith is obtained. The monolith contains a large proportion of cordierite since cordierite has a high resistance to thermal shock. In some embodiments, the monolith is a honeycomb structure. A cross-section of the monolith preferably contains 300-600 channels per square inch. The channels are preferably linear square channels that run from the front to the back of the monolith. At a step 425, the monolith is coated with a layer of the wash coat. This can be achieved by dipping the monolith in the wash coat. The channels of the monolith are also coated with a layer of wash coat. Since the wash coat contains the nano-particles, nano-platinum particles are also on the surface of the monolith. At a step 430, the monolith is dried. At a step 435, the monolith is calcined. The calcination bonds the components of the wash coat to the monolith by oxide to oxide coupling. In addition, the calcination allows the nano-active materials to strongly attach to the nano-supports because the nano-supports have a partially reduced alumina surface. As such, the advanced DOC catalyst is formed.

FIG. 5 illustrates a second inventive process 500 for creating the advanced DOC catalyst in accordance with the present invention. At a step 505, nano-active materials are pinned or affixed to nano-supports, forming nano-materials, by using a high temperature condensation technology such as a plasma gun. In some embodiments, the nano-active materials are gaseous platinum atoms and the nano-supports are some form of alumina, such as aluminum plus oxygen. Since nano-active materials are strongly attached to nano-supports, movement or coalescing/conglomeration of the nano-active materials is limited, prevented, or both. The nano-particles are then combined with a liquid to form a dispersion. At a step 510, a wash coat is obtained. The wash coat is commercially purchased or is made. The wash coat is made by using micron-sized oxides that include alumina and silica. In some embodiments, a certain amount of stabilizers for the alumina and a certain amount of promoters are also added to the wash coat. Typically, there is no difference between the commercially purchased wash coat and the created wash coat. At a step 515, a cylindrical-shaped ceramic monolith is obtained. At a step 520, the monolith is coated with a layer of the wash coat such as via dipping. As such, the channels of the monolith are also coated with a layer of the wash coat. At a step 525, the monolith is dried. At a step 530, the monolith is calcined. At a step 535, the dispersion is applied to the monolith via dipping. At a step 540, the monolith is dried. At a step 545, the monolith is calcined. The calcination bonds the components

of the wash coat to the monolith by oxide to oxide coupling. As such, the advanced DOC catalyst is formed

In order for the wash coat to get good bonding to the monolith, both pH level and viscosity of the wash coat must be in a certain range. Typically, the pH level must be between four and five to achieve oxide-oxide coupling. If the pH level is too low, then the viscosity is too high; as such, the wash coat is a paste instead of a slurry. If the pH level is too high, then the viscosity is too low; as such, even after calcination, the wash coat does not bond to the monolith. Although the use of nanomaterials applied to the advanced DOC catalyst is described, the use of nanomaterials is able to be applied to the DPF and the NOx reduction technology used in the diesel engine. Other catalysts in the automation space are also contemplated.

#### Gas Engines

A gas engine cycles from oxygen rich to oxygen poor (e.g., an oxidizing state to a reducing state). As such, a conventional catalytic converter for gas engines includes an oxidation catalyst and a reduction catalyst. The reduction catalyst is a first stage in the conventional catalytic converter. The reduction catalyst uses platinum and rhodium to help reduce NOx emissions. For example, rhodium catalyzes CO and NO<sub>2</sub> to N<sub>2</sub> and CO<sub>2</sub>. The oxidation catalyst is a second stage in the conventional catalytic converter. It reduces unburned hydrocarbons and carbon monoxide by oxidizing them using platinum and palladium. For example, platinum catalyzes CO and O<sub>2</sub> to CO<sub>2</sub> and catalyzes H<sub>2</sub>C<sub>6</sub> and O<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O. Palladium catalyzes H<sub>2</sub>C<sub>6</sub> and O<sub>2</sub> to CO<sub>2</sub> and H<sub>2</sub>O. The oxidation catalyst aids reaction of the carbon monoxide and hydrocarbons with the remaining oxygen in the exhaust pipe. Accordingly, the gas engine uses a three-way catalytic converter to reduce the three harmful compounds.

Conventional methods of creating the three-way catalytic converter use micron-sized catalytic materials and supports, as discussed above. In addition, the conventional methods use multiple dippings to get palladium ions, rhodium ions, and platinum ions on the monolith since a dip that includes, for example, palladium ions and rhodium ions would produce palladium-rhodium alloys, which is not beneficial in certain conditions and/or applications. Embodiments of the present invention use nano-sized catalytic materials and supports instead. In additions, embodiments of the present invention allows a dip to include palladium ions, rhodium ions, and platinum ions without creating palladium-rhodium alloys, because the different ions have different solid phases.

Methods of creating the advanced three-way catalyst for gas engines are similar to the methods of creating the DOC as discussed above. The difference is in the initial steps 405 and 505 of FIGS. 4-5, respectively. Specifically, instead of using just gaseous platinum atoms in the dispersion, gaseous palladium atoms and gaseous rhodium atoms are also used.

FIG. 6A illustrates a first method of creating the dispersion in accordance with the present invention. Catalyst materials include platinum 615, palladium 620, and rhodium 625. Other catalyst materials are contemplated. Carrier material includes alumina 630. The catalyst materials 615, 620, 625 and carrier material 630 are mixed in a plasma gun. After vaporizing the catalyst materials and carrier material to form a vapor cloud and quenching the vapor cloud, the vapor cloud precipitates nano-particles. FIG. 6B illustrates a nano-particle 600 in accordance with the present invention. The nano-particle 600 comprises a nano-active material 610 and a nano-support 605. Since the plasma gun is extremely chaotic, the catalyst materials form into an alloy. As such, the nano-active material 610 is an alloy. Since a ratio of the nano-active material 610 consisting of platinum, palladium, and rhodium,

depends on an initial ratio of each of the catalyst materials used, different forms of alloys are formed on the nano-support 605. The nano-particles 600 are combined with the liquid to form the dispersion.

FIG. 7A illustrates a second method of creating the dispersion in accordance with the present invention. Instead of mixing platinum 615, palladium 620, rhodium 625, and alumina 630 in the plasma gun, each of the catalyst materials are separately mixed with alumina 630 in the plasma gun. As such, after vaporizing and quenching each of the catalyst materials, three different nano-particles are formed. A collection of the different nano-particles are combined with the liquid to form the dispersion. The three different nano-particles are illustrated in FIG. 7B. A first nano-particle 600' is a platinum nano-active material 635 on the alumina nano-support 605. A second nano-particle 600'' is a palladium nano-active material 640 on the alumina nano-support 605. A third nano-particle 600''' is a rhodium nano-active material 645 on the alumina nano-support 605. A size of the nano-active material is able to be controlled based on a quantity of the nano-active material that was initially placed in the plasma gun. Concentration of each different nano-particle 600', 600'', 600''' is able to be individually and/or collectively controlled.

After creating a dispersion either using the first method (as illustrated in FIG. 6A) or the second method (as illustrated in FIG. 7A), the first inventive process 400 continues at a step 410 and the second inventive process 500 continues at a step 510, as illustrated in FIGS. 4-5, respectively.

While the invention has been described with reference to numerous specific details, one of ordinary skill in the art will recognize that the invention can be embodied in other specific forms without departing from the spirit of the invention. Thus, one of ordinary skill in the art will understand that the invention is not to be limited by the foregoing illustrative details, but rather is to be defined by the appended claims.

We claim:

1. A method of making a catalytic converter comprising: loading feed material into a plasma reactor, the feed material comprising active material and a support material; vaporizing the active material and the support material in the plasma reactor thereby forming a vapor cloud of active material and support material; condensing the vapor cloud of active material and support material, thereby forming solidified nanoparticles comprising nano-active material and nano-support material; and applying a wash coat comprising the solidified nanoparticles comprising nano-active material and nano-support material to a substrate to produce a catalytic converter.
2. The method of claim 1, wherein the nano-active material comprises platinum.
3. The method of claim 1, wherein the nano-active material comprises palladium.
4. The method of claim 1, wherein the nano-active material comprises rhodium.
5. The method of claim 1, wherein the nano-active material is an alloy.
6. The method of claim 1, wherein the nano-support comprises alumina.
7. The method of claim 1, wherein the nano-support comprises a partially reduced alumina surface, the partially reduced alumina surface configured to limit movement of the nano-active material on a surface of the nano-support.
8. The method of claim 1, wherein the feed material comprises a plurality of different active materials.
9. The method of claim 8, wherein the support material comprises alumina.

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10. The method of claim 8, wherein the different active materials include platinum, palladium, and rhodium.

11. The method of claim 1, wherein the wash coat comprises micron sized oxide particles.

12. The method of claim 1, wherein the wash coat comprises micron sized alumina particles.

13. A method of making a catalytic converter comprising loading a first feed material into a plasma reactor, the first feed material comprising first active material and a first support material;

vaporizing the first active material and the first support material in the plasma reactor thereby forming a vapor cloud of first active material and first support material;

condensing the vapor cloud of first active material and first support material, thereby forming solidified first nanoparticles comprising first nano-active material and first nano-support material;

loading a second feed material into a plasma reactor, the second feed material comprising second active material and a second support material;

vaporizing the second active material and the second support material in the plasma reactor thereby forming a vapor cloud of second active material and second support material;

condensing the vapor cloud of second active material and second support material, thereby forming solidified second nanoparticles comprising second nano-active material and second nano-support material; and

applying the first nanoparticles comprising first nano-active material and first nano-support material and the second nanoparticles comprising second nano-active material and second nano-support material to a substrate to produce a catalytic converter.

14. The method of claim 13, further comprising:

loading a third feed material into a plasma reactor, the third feed material comprising third active material and a third support material;

vaporizing the third active material and the third support material in the plasma reactor thereby forming a vapor cloud of third active material and third support material;

condensing the vapor cloud of third active material and third support material, thereby forming solidified third nanoparticles comprising third nano-active material and third nano-support material; and

applying the third nanoparticles comprising third nano-active material and third nano-support material to the substrate.

15. The method of claim 14, wherein at least one of the first support material, the second support material, and the third support material comprises alumina.

16. The method of claim 14, wherein the third active material comprises rhodium.

17. The method of claim 14, wherein the first active material comprises platinum, the second active material comprises palladium, and the third active material comprises rhodium.

18. The method of claim 13, wherein the first active material comprises platinum.

19. The method of claim 13, wherein the second active material comprises palladium.

20. A method of making a three-way catalytic converter comprising:

loading a first feed material into a plasma reactor, the first feed material comprising an oxidation active material and a first support material;

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vaporizing the first oxidation active material and the first support material in the plasma reactor thereby forming a vapor cloud of oxidation active material and first support material;

condensing the vapor cloud of oxidation material and first support material, thereby forming solidified oxidation nanoparticles comprising oxidation nano-active material and first nano-support material;

loading a second feed material into a plasma reactor, the second feed material comprising reduction active material and a second support material;

vaporizing the reduction active material and the second support material in the plasma reactor thereby forming a vapor cloud of reduction active material and second support material;

condensing the vapor cloud of reduction active material and second support material, thereby forming solidified reduction nanoparticles comprising reduction nano-active material and second nano-support material; and

applying the oxidation nanoparticles comprising oxidation nano-active material and first nano-support material, and the reduction nanoparticles comprising reduction nano-active material and second nano-support material to a substrate.

21. The method of claim 20, wherein the oxidation active material comprises platinum.

22. The method of claim 20, wherein the oxidation active material comprises palladium.

23. The method of claim 20, wherein the reduction active material comprises rhodium.

24. The method of claim 20, wherein the oxidation active material is an alloy.

25. The method of claim 20, wherein the first support material comprises alumina.

26. The method of claim 20, wherein the first support material comprises a partially reduced alumina surface, the partially reduced alumina surface configured to limit movement of the nano-active material on a surface of the nano-support.

27. The method of claim 20, further comprising:

loading a third feed material into a plasma reactor, the third feed material comprising second oxidation active material and a third support material;

vaporizing the second oxidation active material and the third support material in the plasma reactor thereby forming a vapor cloud of second oxidation active material and third support material;

condensing the vapor cloud of second oxidation active material and third support material, thereby forming solidified second oxidation nanoparticles comprising second oxidation nano-active material and third nano-support material; and

applying the second oxidation nanoparticles comprising second oxidation nano-active material and third nano-support material to the substrate.

28. The method of claim 27, wherein the oxidation active material comprises platinum, the second oxidation active material comprises palladium, and the reductive active material comprises rhodium.

29. A method of making a two-way catalytic converter comprising:

loading a feed material into a plasma reactor, the first feed material comprising a first oxidation active material and a first support material;

vaporizing the first oxidation active material and the first support material in the plasma reactor thereby forming a vapor cloud of first oxidation active material and first support material;

condensing the vapor cloud of first oxidation material and first support material, thereby forming solidified oxidation nanoparticles comprising first oxidation nano-active material and first nano-support material; and  
applying the oxidation nanoparticles comprising first oxidation nano-active material and first nano-support material to a substrate.

**30.** The method of claim **29**, wherein the first oxidation active material comprises platinum.

**31.** The method of claim **29**, wherein the first nano-support material comprises alumina.

**32.** The method of claim **29**, wherein the first nano-support material comprises a partially reduced alumina surface, the partially reduced alumina surface configured to limit movement of the first nano-active material on a surface of the first nano-support material.

**33.** The method of claim **29**, wherein the first oxidation active material comprises palladium.

**34.** The method of claim **29**, wherein the first oxidation active material is an alloy.

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